A

PROJECT REPORT

On

Liquid Fuel from Oil Seeds by Pyrolysis

Submitted

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CERTIFICATE

It is certified that the work contained in the report entitled **"Liquid Fuel from Oil Seeds by pyrolysis"** by **Saswat Kumar Pradhan**, has been carried out under my supervision.

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ABSTRACT

Demand for energy and its resources, is increasing every day due to the rapid growth in population and urbanization. As the major conventional energy resources like coal, petroleum and natural gas are at the verge of getting extinct, biomass can be considered as one of the best environment friendly renewable energy options. Though there are many thermo-chemical conversion processes like pyrolysis, combustion, gasification, liquefaction, hydrogenation, Pyrolysis has gained special attention as it can convert biomass directly into solid, liquid and gaseous products by thermal decomposition of biomass in absence of oxygen.

In this report, experiments on pyrolysis of sesame seed and groundnut seed was done and effect of temperature on pyrolysis of liquid product, char, volatiles and reaction time were studied. The liquid yield was highest at 500°C for sesame seed and groundnut seed. With increase in temperature, reaction time and weight of char decreased. Volatiles initially decreased and then increased with increase in temperature.

The different FTIR spectra of sesame and groundnut oil show the presence of mostly alkane and alkenes. The results were found consistent when compared with the results of GC-MS.

1H NMR analysis of bio-oil proves that β- CH3, CH_2 hydrogen protons are attached to an aromatic ring in higher proportions.

Presence of pores shown by SEM-EDX analysis paves a path for using this char as an adsorbent.

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CHAPTER - 1

INTRODUCTION

1. INTRODUCTION

From earlier times, we used to depend on plant biomass for our energy demands. When crude oil arrived in the 19th century, it gave a very economical liquid fuel source which industrialized the world and improved standards of living. Energy demand rapidly increased to 50% in 2002 and will increase approximately two and half times the present level [1]. The energy demand is mainly comes from the conventional energy sources like coal, petroleum and natural gas. These sources will be depleted very soon. It is calculated that the petroleum sources will be finished within 2050. As petroleum sources are getting finished, and also there is a demand for petroleum products, so we have to develop economical and energy-efficient processes for the production of fuels [2].

As India is a developing country and energy demand is growing rapidly, exploring and exploiting resources, energy sector reforms and capacity additions are necessary requirements to become a developed country. Because of rapid urbanization, multiplying population and Progressing economy, even after many efforts made in energy supply growth and resource augmentation, India is much behind to meet the increasing energy demands. Energy shortages are affecting hugely to Indian economy as it has to depend on imports.

Biomass can be considered as a potential for the renewable energy sources in near future. It can be defined as living matter on earth. In the biomass solar energy is stored. Biomass is produced by the plants in the process of photosynthesis [3]. Biomass meets 14% of world's total energy need. Chemicals and materials are produced from the biomass. Biomass for energy production mainly comes from forestry products, agricultural crops, biological wastes and agricultural residues, etc. Agricultural products that are easily available produced worldwide and mostly underutilized [4].

Biomass can be converted to energy forms using thermal, biological, and mechanical or physical processes. Biological process is very selective and produces a small number of products in high yield using biological catalysts, thermal conversion gives multiple products, in very short reaction times. Inorganic catalysts are used to improve the product quality. Since thousands of years Pyrolysis has been used for charcoal production but in last 30 years and fast pyrolysis at

around 500 ºC and very short reaction times of up to 2 s .The process directly gives high yields of liquids of up to 75 wt. % which can be used directly in a variety of applications [1]. The three main thermal processes for converting biomass to a more useful energy form is pyrolysis, gasification and combustion. Combustion is a commercial technology which is used in most industrialized and developing countries and mainly developed in resolving environmental problems [2]. Gasification also been used for many years and even if there is many industrial and commercial uses [3, 4] there are very few successful operational units. Fast pyrolysis is an integrated process for production of a liquid fuel which is used directly and also an intermediate pretreatment step to convert solid biomass into a higher energy content transportable liquid for subsequent processing for heat, power, biofuels, and chemicals. This type of process offers a considerable contribution in terms of environmental acceptability, versatility and improved efficiency.

Biomass sources include agricultural crops and their waste by-products, animal wastes, and algae municipal solid waste, wood and wood wastes, waste from food processing and aquatic plants. Biomass resource can be subdivided into different categories. They are mainly

Wastes: Agricultural processing wastes, agricultural production wastes, mill wood wastes, urban wood-wastes, crop residues, and urban organic wastes.

Forest Products: Trees, sawdust, bark, Wood, logging residues, shrubs and wood, etc., from forest.

Energy Crops: Herbaceous woody crops, grasses, short rotation woody crops, starch crops (corn, wheat and barley), sugar crops (cane and beet), oilseed crops (soya bean, sunflower, safflower).

CHAPTER - 2

BIOMASS CONVERSION PROCESSES

2. BIOMASS CONVERSION PROCESSES:

Biomass can be converted in to useful products by mainly two processes they are:

1. Thermo-chemical processes
2. Bio-chemical processes

2.1 THERMO-CHEMICAL PROCESSES:

Thermo-chemical conversion processes have mainly two approaches. First one is the gasification of biomass and its conversion to hydrocarbons. The second process is to liquefy biomass directly by high-temperature, high-pressure, ultra pyrolysis, or supercritical extraction [5]. The main aim of these processes is to convert the waste biomass into energy rich useful products. Types of thermo-chemical conversion processes are:-

a. Combustion
b. Gasification
c. Liquefaction
d. Hydrogenation
e. Pyrolysis.

2.1 PYROLYSIS:

Pyrolysis is mainly concerned with thermo-chemical process for conversion of biomass. It involves heating the biomass at high temperature in absence of air which produces gaseous products and later can be condensed to give liquid fuels consisting of pyrolytic oil or bio-oil and oily water (mixture of water and certain hydrocarbons). In a good operational condition almost 70-80% of gaseous products are converted to liquid fuels which later can be modified according to its use. This process is a very popular process which makes a good quantity of liquid fuel from biomass, which is very similar to commercial transportation fuels and can be upgraded or modified to replace transportation fuel. It also provides some amount of gaseous and solid

products which have higher market value as they can also be used as a source of energy. Longer vapor residence times and Lower process temperatures favor the production of charcoal. Longer residence times and High temperatures increase biomass conversion to gas, and short vapor residence time and moderate temperatures are optimum for producing liquids. Mostly three products are always produced, but the composition can change over a wide range by adjustment of the process parameters.

Biomass decomposes rapidly to produce mostly vapors and aerosols and some charcoal and gas. When cooling and condensation takes place, a dark brown homogenous mobile liquid is formed which has a heating value about half that of conventional fuel oil. With most biomass feeds low in ash a high yield of liquid is obtained. The features of a pyrolysis process for producing liquids are:

1. Very high heating rates and heat transfer rates at the biomass particle reaction interface favors a finely ground biomass feed of typically less than 3 mm as biomass generally has a low thermal conductivity.
2. Controlled pyrolysis reaction temperature of around 500 ºC to maximize the liquid yield for most biomass.
3. Vapor residence times of typically less than 2 s to minimize secondary reactions.
4. Product char is removed to minimize cracking of vapors.
5. Pyrolysis vapors are rapidly cooled to give the bio-oil product.

Pyrolysis for liquids takes less time, phase transition phenomena and heat and mass transfer processes, as well as chemical reaction kinetics, play important roles. The reacting biomass particles are brought to the optimum process temperature also to minimize their exposure to the lower temperatures that favor formation of charcoal. Small particles can be used, for example in the fluidized bed processes. Heat is transferred very fast only to the particle surface that contacts the heat source which is used in ablative processes. Main product which is bio-oil, is obtained in yields of up to 75 wt. % on a dry-feed basis, together with by-product char and gas which is used within the process to provide the process heat requirements so that there are no waste streams other than flue gas and ash. Liquid product depends on hot vapor residence time , biomass ash content, biomass type, temperature, hot vapor residence time and char separation. In pyrolysis

process the material is dried to less than 10% water in order to minimize the water in the product liquid oil, the feed is grinded to give sufficiently small particles to ensure rapid, fast and efficient separation of solids (char), and rapid quenching and collection of the liquid product (often referred to as bio-oil).Any form of biomass can be considered for fast pyrolysis. Maximum work has been done on wood and more than 100 different biomass types already been tested by many laboratories, olive pits and nut shells to energy crops such as miscanthus and sorghum, from agricultural wastes such as straw, forestry wastes such as bark and solid wastes such as sewage sludge and leather wastes.

A commercial process constitutes three main stages from feed to delivery of one or more useful products:

1. Feed, storage, handling, preparation and pretreatment;
2. Fast pyrolysis to a more usable form of energy in liquid form which is known as bio oil;
3. Liquid product is converted by refining, processing and can be used as electricity, heat, and chemicals.

The advantage of pyrolysis is because it can convert biomass directly into liquid, gaseous products and solid by thermal decomposition of biomass in the absence of oxygen [6]. Pyrolysis is of two types. They are

a. Slow Pyrolysis
b. Fast Pyrolysis

2.2 BIO-CHEMICAL PROCESSES:

Bio-chemical processes which include anaerobic digestion and alcoholic fermentation are mainly employed for energy conversion of biomass with high moisture content such as animal manure and bio-waste. These processes are based on biological actions that convert semi-solid or liquid biomass into a biogas or liquid fuel (i.e. ethanol) [7].

2.2.1. ANAEROBIC DIGESTION

Anaerobic digestion is the degradation of organic wastes through microbial actions in the absence of oxygen to produce reducing gases (biogas) which mainly composed of methane, carbon dioxide and contains trace components which is hydrogen sulfide, acids and thiols. One example is the landfill gas (LFG) buried in sanitary landfill sites. LFG, which consists of up to 50% methane, can be purified and then burned in engines or turbines to produce heat and electricity [8].Biogas is generally produced from animal manure in an airtight container (digester). Because of high heating Value (5400–6000 kcal/Nm^3) of biogas, the biogas can be directly used in burners, also can be used as gas fuel in internal combustion engines to generate electricity, or can be upgraded to natural gas quality by the removal of carbon dioxide and hydrogen sulfide.

2.2.2. ALCOHOLIC FERMENTATION:

Fermentation is applied in the production of alcoholic wines from sugar crops and starch crops Ethanol can be produced from biomass material in the presence of organisms (e.g. yeast) that gives a high quality fuel for storage and transport [8]. Biochemical conversion of wastes is more difficult for the fermentative degradation and need first to be broken down by acidic or enzymatic hydrolysis because of the presence of longer-chain polysaccharides. Product ethanol after distillation purification can be used as a supplement or substitute for petrol. Biomass materials for alcoholic fermentation are generally agricultural production/processing residues. Molasses which is a by-product of sugar-manufacturing process has been industrially bio-converted for the production of ethanol.

CHAPTER - 3

LITERATURE REVIEW

2. LITERATURE REVIEW:

Renewable energy sources are a high priority for many countries and will play a major role in the chemical industry in the near future. Renewable energy sources becoming popular for their lack of environmental risks and pollution; they are alternatives to fossil fuels and their derivatives. They are more evenly distributed over earth's surface than fossil fuels or uranium and may be exploited using less capital. Hence renewable energy sources increase decentralization of energy supplies and energy is supplied all top to bottom level [1]. Lignocellulosic biomass is one of the promising renewable feedstock for production of biofuels and chemicals because of petroleum shortage, high price of the crude oil and environmental pollution. This is a renewable raw feedstock for conversion into liquid and gaseous fuels, chemical products and other energy-related products [2].Biomass as a feedstock is required for bio-fuel, which shows very different properties than traditional fossil fuels and their derivatives [3].Lignin–cellulosic materials are reactive and more volatile than coals. Biomasses vary in volatile matter concentration; as biomass can change in composition based on the climatic conditions and seasonal variation. Chemical composition of biomass affects the conversion processes differently. As high nitrogen and ash concentration reduces hydrocarbon yield during thermochemical conversion [2].Lignin concentration, one of the components of lignocellulosic material does not have a detrimental effect on thermochemical product yield [4]. Biomass compositions determine the yield from a biochemical conversion, and thereby have a significant effect on conversion process economics. The impact of biomass characterization on the expanding biofuel and bio product industry can be seen. These complex biomass compositions and thermal behavior in conversion processes, yield is predicted. Mathematical models is created for economic analysis, understand products. Importantly technology is created to make conversion processes more efficient than fossil fuel. Biomass is considered to be a promising renewable energy. The biomass availability in the world is 220 billion oven-dry ton (odt) per year or 4500 EJ (1018 J) [5]. It is the world's largest and most sustainable energy resource. If we can increase the capacity of energy produced from biomass we will be able to reduce the fossil fuel consumption. The benefits of this process are to reduce the greenhouse gases in comparison to fossil fuels. It also solves the dependence of imported fossil fuels for many countries [5]. Biomass refers to plant derived organic matter that

is available on a renewable basis. Lignocellulosic biomasses are energy crops residues agricultural crop waste, forest residues, aquatic plants etc. and are about 50% of the all biomasses. It is composed of cellulose, hemicellulose, and lignin. Cellulose is made of monomers of glucose, a six sugar linked by b (1–4) glycoside bonds. Lignin is a macromolecular in nature with phenolic character; it is helical and contains ether and carbon–carbon linkages. Hemicellulose is a branched carbohydrate and is composed of both hexose and pentose sugar. Currently, lignocellulosic biomass resources deserve major interest to produce bio oil, hydrogen bioethanol and chemicals.

Bio-oils have already been used in turbines, boilers and engines. It is also upgraded to high quality hydro carbon fuels although financial cost is high [1]. Pyrolytic oil can be stored for a longer duration; therefore can be made available when necessary. Transportation of pyrolytic oil is very easy. The pyrolytic from non-food related biomass is a second generation bio-fuel and therefore does not affect the food industry. It can also be used in applications where it substitutes for crude oil. Many oil containing seeds are available in forest, which can be used to produce bio-fuel. Bio-fuels can be used in internal combustion, jet or steam engines to provide power to move everything from pistons to turbines. Slow pyrolysis is also called as conventional pyrolysis. Literatures revels that in slow pyrolysis the yield of oil is less and char yield is more [2, 3]. The production and the application of the bio-oil can take place at different locations and different moments in time.

Pyrolysis gives all three types of pyrolysis product (gas, liquid, and char). To know the effect of temperature on the product distribution the slow pyrolysis of pomegranate seeds was carried out by Suat and Selhan at 400, 500, 600 and 800 ºC. The bio-chars produced from pomegranate seeds having carbon rich fuels with high bulk densities and calorific values and The maximum liquid yields were obtained at the temperatures of 500 and 600 ºC [4]. To determine particularly the effects of heating rate, pyrolysis temperature, particle size on the pyrolysis product yields and their chemical compositions Beis et al. studied the pyrolysis behavior of safflower seed in fixed-bed pyrolyzer and obtained the maximum oil yield of 44% at temperature of 500 ºC, particle size range of +0.425– 1.25 mm, with heating rate of 5 ºC/min and sweep gas (N_2) flow rate of 100 cm^3/min [5]. To investigate the effects of pyrolysis temperature Safflower (Charthamus

tinctorius L.) Sensoz et al. pyrolyzed seed press cake by a fixed-bed reactor at a temperature of 400 to 600 ºC at different heating rate (10, 30, 50 ºC/min) under the sweep gas of $N_2$with a flow rate of 100 cm^3/min, heating rate and sweep gas flow rates on the yields of the products and obtained the maximum yield of bio-oil 36% by weight at 500 ºC with a heating rate of 50 ºC/min under the sweep gas of N_2 with a flow rate of 100 cm^3/min due to the decrease in mass transfer limitations [6]. Putun et al. used clinoptilolite catalyst at different conditions and investigated the effect of catalyst, pyrolysis temperature and sweeping gas flow rate and concluded that maximum 30.84% of liquid yield at temperature of 550 ºC, sweeping gas flow rate of 100 cm^3/min in the presence of clinoptilolite catalyst (20% based on raw material) [7]. In a fixed bed stainless steel reactor from temperature 450 to 850ºC under static atmosphere at rates of 15 ºC/min and 25 ºC/min Rapeseed cake was pyrolyzed by Karaosmanogi and Culcuogi towards understanding the influence of heating rate and pyrolysis temperature on product yield. The maximum yield was obtained at 650 ºC at a heating rate of 15 ºC/min [8].In a fixed-bed reactor, Pyrolysis on soybean cake was carried out by Putun et al. under nitrogen and steam atmosphere and obtained the maximum yield of oil 33.78% at 550 ºC of particle size $0.850 > Dp < 1.250$ mm when sweeping gas (N_2) flow rate was 200 cm^3/min and the oil yield increased to 42.79% with a steam velocity of 1.3 cm/s. The gas products obtained from the pyrolysis of rapeseed oil cake carried out by Suat et al. in a fixed-bed reactor at 500 ºC, mainly consisted of CO_2, CO, CH_4 and H_2S gas and liquid contains 2,3,5-trimethoxy toluene, toluene, oleic acid, 1H-indole,psoralene, phenol,(Z)-9-octadecanamide and phenol derivatives. The water phase composed of both aromatic hydrocarbon and nonaromatic compounds and gave the conclusion that at all temperature the liquid having same calorific value [10]. Sensoz et al. on Brassica napus L. In a Heinze reactor at a temperature of 500 ºC at 40ºC/min of heating rate with a particle size of range of 0.224–1.8 mm, maximum 46 wt. % oil obtained with a particle size range of 0.85–1.8 mm with a heating value of 38.4 MJ/kg. Onay et al. performed pyrolysis on rapeseed in a free fall reactor at atmospheric pressure under nitrogen atmosphere to investigate the effect of particle size ,final pyrolysis temperature and sweep gas flow rate on the yields of products and resulted that the maximum pyrolysis conversion of 78% at a temperature of 700 ºC. The maximum bio-oil yield of 75% was obtained at a final pyrolysis temperature of 600 ºC, particle size range of 0.224– 0.6 mm and the sweep gas flow rate of 100 cm^3/min [12]. Putun et al. studied pyrolysis of pistachio shell and concluded that the highest bio-oil yield with a value of 27.7% at a

temperature of 773 ºK, when the heating rate and carrier gas flow rate were as 300 ºK/min and 100 cm^3/min respectively. Cao et al. studied the pyrolysis of waste corncob and got a faster rate of production at a temperature range of 350–400 ºC and a slower at 400–600 ºC whereas the yield of the liquid was nearly constant [14]. Zhongyang et al. investigated the pyrolysis behavior of different wood samples at temperature of 773 K in a fluidized bed reactor with a feed rate of 3 kg/h at atmospheric pressure and inert atmosphere and concluded that the higher ash content of biomass decreases the yield as well as the quality of bio oil [15]. Omar et al. carried out experiment on Ellajjun oil shale to know the effect of particle size on product components and observed that the yield of bio oil decreases with increase in particle size [16].Using quartz fluidized fixed-bed reactor Pyrolysis of oil palm Empty Fruit Bunches (EFB) study was done by Mohamad Azri et al. The effects of pyrolysis particle sizes, temperatures and heating rates on the yield of the products were investigated. The temperature of heating rate and pyrolysis were varied in the range 300–700 ºC and 10–100 ºC/min respectively. The result shows that the maximum bio-oil yield was 42.28% obtained at 500 ºC, with a heating rate of 100 ºC/min and particle size of 91–106 lm [17]. Goh Meng et al. investigated the pyrolysis behavior of oil palm shell in a fluidized bed reactor at temperature of 450 ºC in presence of nitrogen gas and concluded the pyrolytic oil was rich in phenolic compounds [18]. Fluidized bed flash pyrolysis experiments have been conducted by Antony Raja on jatropha oil cake to determine particularly the effect of nitrogen gas flow rate, particle size and temperature on the pyrolytic yield and obtained maximum liquid yield of 64.25% at temperature of 500 ºC with a particle size of 0.7–1.0 mm and at a nitrogen gas flow rate of 1.75 m3/h [19]. Liquid product is characterized for to their functional group presents, elemental analysis and fuel properties which show that the pyrolytic oil can be a substitute for bio-fuel.

Bio-oils are usually dark brown, free-flowing liquids having a smoky odor. Physical properties of bio-oils are given in different publications [10-12].These different properties are due to the chemical composition of the oils, which is different from that of petroleum oils. Bio-oils are mixtures comprised of different size molecules derived primarily from depolymerization and fragmentation reactions of three key biomass building blocks:hemicellulose, cellulose and lignin. Therefore the elemental composition of bio-oil resembles that of biomass rather than that of petroleum oils.

An even more important consequence of the organic oxygen is the instability of bio-oil. The oxygen content of bio-oils is usually 35-40 wt. %. This oxygen is in most of the 300 compounds in the oils. The distribution of compounds depends on the biomass used and on the process (residence time, and heating rate profiles, temperature). Increase in pyrolysis reduces the organic liquid due to cracking of the vapors and formation of gases but leaves the organic liquid with less oxygen. The single most bio-oil component is water. The other compounds are hydroxyketones, sugars, carboxylic acids, hydroxyaldehydes, and phenolics. Most of the compounds are present as oligomers with a molecular weight ranging from 900 to 2500.Oxygen in oil components is the main differences in the properties seen between biomass pyrolysis oils and hydrocarbon fuels.

Water content varies over a wide range (15-30%) depending on the feedstock. At this concentration, water is usually miscible with the oligomeric lignin-derived components because of the solubilizing effect of other polar hydrophilic compounds (hydroxyaldehydes,low-molecular-weight acids, alcohols, and ketones) mostly originating from the decomposition of carbohydrates. The water has both positive and negative effects on the oil properties. Water lowers its heating value, the LHV and flame temperature. Water contributes to the increase in ignition delay and in some cases to the decrease of combustion rate compared to diesel fuels. On the other hand, it improves bio-oil flow characteristics (reduces the oil viscosity), which is beneficial for combustion (pumping and atomization). Water leads to a more uniform temperature profile in the cylinder of a diesel engine and to lower NO*x* emissions.

For their chemical composition, bio-oils exhibit a wide range of boiling temperature. Besides water and volatile organic components, biomass pyrolysis oils contain good amount of nonvolatile materials such as sugars and oligomeric phenolic. The slow heating of the oils during distillation results in polymerization of some reactive components. The oils start boiling below 100 °C but the distillation stops at 250- 280 °C, leaving 35-50% of the starting material as residue. So bio-oils cannot be used for applications requiring complete evaporation before combustion.

The viscosity of bio-oils can vary over a wide range (35-1000 cP at 40 °C) depending on the process conditions and feed stock, and especially on the efficiency of collection of low boiling

components. The viscosity of bio-oil decreases at higher temperatures much faster than that of petroleum derived oils, so it can be easily pumped after a moderate preheating. Viscosity reduction can also be achieved by addition of polar solvents such as methanol or acetone. The disadvantage is that when the oils are stored or handled at higher temperature the viscosity increases with time. It is believed that chemical reactions among various compounds present in the oil, leads to the formation of big molecules. Also there is evidence that bio-oil reacts with oxygen from air.

Bio-oils contain good amount of organic acids which is acetic and formic acids, that results in a pH of 2-3.The oils are corrosive to construction materials such as carbon, steel and aluminum. The corrosiveness of bio-oil is especially severe at high temperature and increased water content. The bio-oils are noncorrosive to stainless steels. Polyolefins materials are not acceptable for construction where other circumstances permit.

Combustion Behavior properties have an effect on the bio-oils during combustion. It also has an effect for energy production in standard equipment. Bio-oils are combustible in nature but not inflammable. Due to the high content of nonvolatile components, bio-oil needs more energy for ignition. When once ignited, bio-oil burns with a stable flame. A detail study on the fundamentals of bio-oil combustion was carried out at Sandia National Laboratory with the bio-oils produced at the NREL vortex reactor plant [18, 19]. Combustion tests on single droplets shows a very unique, multiple process comprised of the following phases: droplet micro-explosion, disruptive burning of the droplet fragments, ignition, quiescent burning (blue), and formation and burnout of cenosphere particles. Petroleum distillate fuel oil shows in the same conditions only sooty burning from ignition through burnout. The burning duration of bio-oils are comparable to those of No. 2 fuel oil under the same conditions in spite of large differences in fuel properties and combustion mechanisms. The droplets of less cracked pyrolysis oils were found to show an earlier micro-explosion and longer burnout times than No. 2 fuel oil. The bio-oils which undergo more cracking in the pyrolysis process shows more violent micro explosions. This resulted in more rapid burnout than other fuel oil. The adiabatic flame temperature for bio oil is high, 1700-2000 ºK as compared to 2200- 2300 ºK for other fuels. This difference is much less on the basis of heating values because of significantly lower stoichiometric air-to-fuel ratios

For pyrolysis oils. Macro-scale combustion tests performed in flame tunnels at MIT20 and CANMET21 on fast pyrolysis bio-oil as well as those done at the International Flame Research Foundation, ENEL, and COGIS24 using slow pyrolysis liquid did not indicate fundamental differences in combustion behavior of No. 2 fuel oil and wood pyrolytic oil and confirmed that bio-oil can burn with stable flames quite similar to that of petroleum-based fuel oils. Gas emissions from bio-oil showed higher particulate, CO levels than that of petroleum fuels with NO*x* concentration much less than that of No. 6 but more than for No. 2 fuel oil.

Biomass is pyrolysed at slow heating rates (5–7 ºK/min). This leads to less liquid and gaseous product and more of char production. Much amount of work already done on this process.
S. Sensoz, etal,[22]conducted pyrolysis on Brassica apus L to study the effect of particle size and yields in a Heinze reactor under static atmosphere at a temperature of 500^{o}C at 40^{o}C/min of heating rate with a particle size of range of 0.224-1.8 mm. Maximum 46 wt% oil obtained with a particle size range of 0.85-1.8 mm with a heating value of 38.4 MJ/kg. FilizKaraosmanogiluetal, [6] conducted pyrolysis on Rapeseed cake in a fixed bed stainless steel reactor from temperature 450-850°C under static atmosphere at rates of 15°C/min and 25°C/min towards understanding the influence of heating rate and pyrolysis temperature on product yield. The maximum yield was obtained at 650°C at a heating rate of 15°C/ min. Putun et al.[17] conducted pyrolysis in a fixed bed reactor for sunflower presses bagasse , sunflower presses bagasse, Euphorbia rigida, and hazelnut shell, at different temperatures and heating rate of 7 K/min. Product yield increased in all the three cases when the pyrolysis temperature was increased from 673 to 973 Pyrolysis of cottonseed was conducted by Ozbay et al.[13]cake at heating rates of 7 ^{0}C /min in a two reactors, Heinz reactor and a well-swept tubular reactor. It was found that with the increase in temperature the oil yield increased up to 600 ^{0}C but decreased at around 750 ^{0}C. Onay et al. [14] conducted pyrolysis of rapeseed in a well-swept fixed bed reactor. Oil yield was obtained as 68% with pyrolysis temperature of 550 ^{0}C, particle size 0.6–0.85 mm, heating rate of 300 ^{0}C /min and N_2 flow of 100 cm^3/min.Beis et al.[2]conducted pyrolysis of safflower seed with heating rates of 5 ^{0}C /min at different flow rates. Oil yield was highest at 550 ^{0}C for all particle sizes and flow rates. Gas yield found highest at 700 ^{0}C. Putun E. etal,[17] conducted pyrolysis on soybean cake in a fixed-bed reactor under nitrogen and a maximum yield of oil 33.78% was obtained at 550°C of particle size 0.850-*D*p-1.250 mm when sweeping gas (N_2) flow rate was 200 cm3/min and the

oil yield increased to 42.79% with a steam velocity of 1.3 cm/s. Onay and Kockaretal,[14]conducted experiments on pyrolysis of rapeseed to investigate the effect of particle size, temperature, heating rate and sweep gas flow on the product yield. Results showed that char yield decreased from 27% to 14.5% with the increase in the temperature. Maximum oil yield of 73% was obtained at temperature of 550–600 ^{0}C, particle size of +0.6–1.25 mm, and sweep gas flow rate of 100 cm^3/min.Putun E, Uzun BB(2005)[18] conducted pyrolysison cotton-seed cake with clinoptilolite catalyst at different temperature and sweeping gas flow rate and found that maximum 30.84% of liquid yield at temperature of 550^{o}C, sweeping gas flow rate of 100 $cm^{3/}$min NurguOzbayetal, [12] conducted pyrolysis on cotton seed cake in a fixed bed reactor to determine the effects of pyrolysis temperature, heating rate and sweep gas flow rate. Maximum oil yield of 34.8% was obtained at final temperature of 550^{o}C with a heating rate of 700^{o}C/min and nitrogen flow rate of 100cm^3/ min. Basak B. etal [1] conducted pyrolysis on pistachio shell and concluded that the highest bio-oil yield with a value of 27.7% at a temperature of 773 K. when the heating rate and carrier gas flow rate were as 300 K/min and 100 cm^3/ min. Beis S.H. [2] conducted pyrolysis on Safflower seed press cake in a fixed-bed reactor from temperature 400-600^{o}C at different heating rate (10, 30, 50^{o}C/min) under the sweep gas of N_2 with a flow rate of 100 cm3/min. The results showed that the maximum yield of bio-oil was 36% by weight at 500^{o}C with a heating rate of 50^{o}C/ min under the sweep gas of N_2 with a flow rate of 100cm^3/min.

Global use of energy has been growing faster than the world population. The development of energy sources is not keeping pace with spiraling consumption. The world major energy demand is provided from the convectional energy sources such as coal, oil, natural gas and so on. The life of all the convectional fuels is limited by the present and foreseeable future energy consumption of the world. So the attention is being given to new and renewable energy sources such as wind, thermal, solar, hydroelectric, biomass and so on. Electricity production based on fossil or nuclear fuels requires more cost whereas the use of renewable energy sources may involve lower costs .Energy is one of the major sources of pollution in any developing country. It is well known that SO_2 emissions from the use of fossil fuels are the main cause of acid rain. On a wide scale, increase in the greenhouse gases presents a threat to the world climate. Over the last fifty years, there appeared a continuous increase in the average temperature values up to a half degree

centigrade. If this continues, some extreme events are expected in some areas of the world, as excessive rainfall and floods, droughts and local imbalances, in the natural climate behaviour, giving rise to unusual local heat and cold. With increasing energy demand the emerging alternative and renewable energy resources are expected to take an increasing role in energy scenario of the future energy needs, in order to reduce the environmental concerns and impacts with regard to air and water quality, acid rain, global warming and so on. Renewable biomass is now being considered as an important energy resource all over the world and for an agriculture based economy like India, to convert widely available biomass materials into various forms of fuel is most attractive. Biomass is used to meet a variety of energy consumption, including fueling vehicles, generating electricity and providing process heat for industrial facilities. Energy from biomass is attractive on a number of counts; firstly its primary source is free or of low value and then plants absorb solar energy and fixes atmospheric CO_2 by photosynthesis. It is the only renewable source of carbon that can be converted into convenient liquid, gaseous solid and gaseous fuels through different conversion processes. Biomass has a good potential by giving annually renewable sources to replace the liquid hydrocarbons used mainly for transportation. So both developing and industrialized nations require new technologies, which generally utilize the biomass resources. Many conversion processes are used to convert the biomass into higher value fuels. The conversion technologies used are biochemical and thermochemical. The thermochemical processes include pyrolysis, combustion and gasification. Among all of these, pyrolysis is considered as an important thermochemical fuel conversion process. The pyrolytic oil is of particular interest since it can be stored and transported but it has to be used at or near the process plant. The oil is used directly as a liquid fuel which is added to petroleum refinery feedstock or catalytically upgraded to fuels.

The life of convectional fossil fuels has become limited in recent scenario, and the use of energy and their source has been growing faster than the world population. The use of fossil fuels increased five times more than the use of renewables in the last three decades. Increase in the emissions rates of greenhouse gases produced from the use of these fossil fuels presents a threat to the world climate. There is a need to develop energy-efficient processes which is economical for the production of fuels and chemicals. Biomass is mostly used in solid form and in the form of liquid fuels, renewable municipal solid waste and gas. It has been a major source of energy in

the world since the beginning of civilization. The urgent need for reductions of the greenhouse gas emissions may provide a significant incentive to develop bio energy. Biomass can act both as a carbon sink and a substitute for fossil fuels. Biomass for energy production has a special place among all other renewable energy sources and it is estimated to contribute with 10–14% to the world's total energy supply. Though there are many biomass conversion processes like pyrolysis, gasification, liquefaction, combustion and hydrogenation. Pyrolysis has gained special attention as it can convert biomass into solid, liquid and gaseous products by thermal decomposition in absence of oxygen. The liquid product generated by the pyrolysis of biomass may also be upgraded to good quality fuels and added to petroleum fuels or may contain chemicals in economical recoverable concentrations. Sesame and mustard seed contains 42–49% and neem seeds contain 15.4–25.4% of seed oil. The production of sesame and mustard seeds is 0.76 and 6.32 million tons for the year 2009–2010 respectively and there are 14 million neem trees growing in India. Trees have the capacity to yield 3.5 million tons of neem seed per year. From 1 kg of sesame, mustard and neem seeds, 320–350 and 200–230 g of seed oil can be extracted by mechanical pressing and the left over is the residue that can be further used as a source of biomass. There have been many recent studies on the pyrolysis of oil cakes. Ozbay et al. [13] studied the thermal pyrolysis of cotton-seed cake in two different reactors to investigate the effect of temperature on product yields and chemical composition. Putun et al. [17] conducted experiments on pyrolysis of cotton-seed cake by using zeolite as catalyst in steam atmosphere to study the effect of temperature on pyrolysis yields. Putun et al. [17] carried pyrolysis experiments of cotton stack in Heinze-type reactor by varying temperature (400–700 ºC), particle sizes ranging from 0.25 mm to 1.8 mm in nitrogen gas flow rate. Putun et al. [17] conducted slow pyrolysis of soybean cake in a fixed bed reactor to study the factors effecting yield of liquid product by varying particle size in steam and nitrogen atmosphere. Sensoz et al.[22] studied thermal pyrolysis and characterization of safflower seed press cake in a fixed bed reactor. Raja et al. conducted flash pyrolysis experiments in a fluidized bed reactor by using jatropha oil cake to determine the effects of pyrolysis temperature, particle size and nitrogen gas flow rate on the product yields. Putun et al. [17] pyrolyzed olive residue in a fixed bed reactor to determine the role of final sweeping gas flow rate, temperature and steam velocity on the product yields and liquid product composition with a heating rate of 7 ºC min^{-1}. More extensive work was done on pyrolysis of rapeseed cake.

Pyrolytic bio-oil, having a number of draw-backs, typically its acidic nature(pH 2.5-3.4), contains substantial amount of water 20-30%, ash 0.04-0.24% and its viscosity ranging between 35 to 53 CSt at 400ºC. Scott et.al reported about formic acid and acetic acids in fast pyrolysis products between 0.4-7.2% and 2.1-6.1% r depending on feeds stocks. In addition to all these, bio-oil has low calorific value than diesel because of water and oxygenates. This structural water disables it, in mixing with hydrocarbon based diesel oil. This also contains suspended char originating from pyrolysis which becomes a reason for particulate emission due to slow burning of the oil. So bio-oil are difficult to use as it may corrode the delivery system and storage tank. As the alkali content is present the oil during storage tends to polymerize making the liquid viscous. Raveendran et. al has development co-relation showing the effect of lime and potassium in presence of lignin on the change in the volatile fraction.

CHAPTER - 4

MATERIALS AND METHODS

4. MATERIALS AND METHODS:

4.1 Collection of the agro materials:

Three raw materials sesame seed and groundnut seed have been collected in the form of seed from the nearest store as they are used for cooking purpose.

4.2 Characterization of raw material

4.2.1 Proximate Analysis

It provides information on moisture content, ash content, volatile matter content and fixed carbon content of the material. Fixed carbon other than ash does not vaporize when heated in the absence of air. Fixed carbon is usually determined by subtracting the sum of the first three values that is moisture, ash, and volatile matter (weight percent from 100 percent).So, it is very important for economic reasons to know the moisture and ash contents of the material. They do not contribute to the heating value of a coal. In most cases ash is an undesirable residue also a source of pollution. In some purposes (use as a chemical feedstock, liquefaction) the presence of mineral matter may be needed. Mostly heat value of the material comes from after excluding moisture, volatile matter, and fixed carbon content. For most of the material it is necessary to measure the actual amount of heat released after combustion (expressed in kilojoules per kilogram or British thermal units per pound).It was carried out using ASTM D3172 - 07a method.

4.2.2. Ultimate Analysis

Ultimate analysis is performed to determine the elemental composition of the material. Ultimate analyses are used to determine the carbon, hydrogen, nitrogen, sulfur, ash, oxygen contents of the material. For the specific applications, other chemical analyses can be employed. These include identifying the forms of sulfur present. Sulfur occurs in the form of sulfide minerals, sulfate minerals, or organically bound sulfur. Other specific cases the analyses may involve determining the trace elements present which influence the suitability of the material for a particular purpose. This may include methods for reducing environmental pollution and so forth.

It was carried out using a CHNSO elemental analyzer (Variael CUBE Germany) which provides carbon, hydrogen, nitrogen, sulphur percentage composition. And when sum of theses compositions is subtracted from 100, it gives oxygen percentage composition.

4.2.3 Calorific Value

Calorific value of a material is the amount of heat liberated when 1Kg of that material is burnt. The calorific value is very important in calculating the competitiveness of a processed fuel in a market situation. Other factors, such as ease of handling, burning characteristics also influence the market value. But calorific value is probably the most important factor. It should be recognized when selecting the raw material. It was determined for both seed and char using a bomb calorimeter (Model: AC-350, LECO Corporation USA).

4.2.4 Thermo-Gravimetric Analysis

Thermo gravimetric analysis or thermal gravimetric analysis is mainly considered as a type of testing on samples which determines changes in weight to a temperature program in a controlled atmosphere. It relies on a high degree of precision in two basic aspects which is weight and temperature. As most weight loss curves look more or less similar, the weight loss curve may require keen analysis before results may be interpreted. A derivative weight loss curve can identify the point where weight loss is most prominent. Interpretation is limited without further modifications of the overlapping peaks. For the determination of the composition and purity one must take the mass of the substance in the mixture by using thermal gravimetric analysis. Thermal gravimetric analysis is a process which involves heating a mixture to a high enough temperature so that one of the components decomposes into a gas that dissociates into the air. Thermo gravimetric analysis is a process which utilizes heat and stoichiometry ratios to determine the percent by mass ratio of a substance. If the compounds in the material remain known, then the percentage by mass is determined by taking the weight of what is left in the mixture and dividing it by the initial mass. After knowing the mass of the original mixture, the total mass of impurities liberating upon heating then the stoichiometric ratio can be used to calculate the percent mass of the substance in a sample. TGA is used in research and testing to determine characteristics of materials such as absorbed moisture content of materials, the level of

Inorganic and organic components in materials, polymers, to determine degradation temperatures, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

The analyzer consists of a high-precision balance with a pan of platinum loaded with the sample. Pan resides in a furnace and is heated or cooled during the experiment. Different process using a quartz crystal microbalance is devised for measuring smaller samples on the order of a microgram versus milligram with conventional TGA. Sample is placed in a small electrically heated oven with a thermocouple for accurate measurement of the temperature. The atmosphere may be supplied with an inert gas to prevent oxidation or other undesired reactions. A computer is employed to control the instrument.

Pyrolysis is heating of a substance in absence of air at a particular temperature. Therefore, the temperature for effective pyrolysis of the oil seeds has to be determined. For this purpose, thermo-gravimetric analysis (TGA) of the sample seed was done using a DTG60 instrument. Around 20-30 milligrams of sample seed was taken and heated up to a final temperature of 800°C and a residence time of 1 minute at 800°C was allowed. TGA was performed at a heating rate of 25°C/Min and one observation was taken at a heating rate of 10°C/Min in air medium. Thermo-gravimetric weight loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation of oil seeds takes place.

4.3 Experimental set up for pyrolysis:

Fig 1.shows the schematic diagram of the pyrolysis experimental set-up. The main units of the pyrolysis reactor set-up are the furnace, pyrolysis reactor and vapor condensing unit. The reactor is cylindrical shaped vessel made up of stainless steel having capacity of ½ liter. The rector which contains the feed is inserted vertically in to an electrically heated furnace. The feed was pyrolyzed at each run and the vapors generated from the rector were condensed in a water cooled condenser. The condensed liquid was collected in a measuring cylinder. The residue (char) in the reactor is known as pyrolytic char. The residue char was usually collected after cooling the

reactor. The temperature of the furnace is maintained by a highly sensitive PID controller. The heart of the setup is the electrically heated furnace. In this furnace, one can attain as high as temperatures of 1200^{o}C.

Fig 2.shows the schematic diagram of the pyrolysis experimental set-up for a larger quantity of biomass. The main units of the pyrolysis reactor set-up are the furnace, pyrolysis reactor, vapor condensing unit, stirrer motor, pressure Gauge, temperature and motor control. The reactor is cylindrical shaped vessel made up of stainless steel having capacity of 3 liter. The feed is generally inserted through the reactor by rotating the extruder. The feed was pyrolyzed as a continuous batch process and the vapors generated from the rector were condensed in a water cooled condenser. The condensed liquid was collected in a large container of 2 to 3 liter. The residue char was usually collected after cooling the reactor. The temperature of the furnace is maintained by a highly sensitive PID controller. The heart of the setup is the electrically heated furnace. In this furnace, one can attain as high as temperatures of 1500^{o}C.

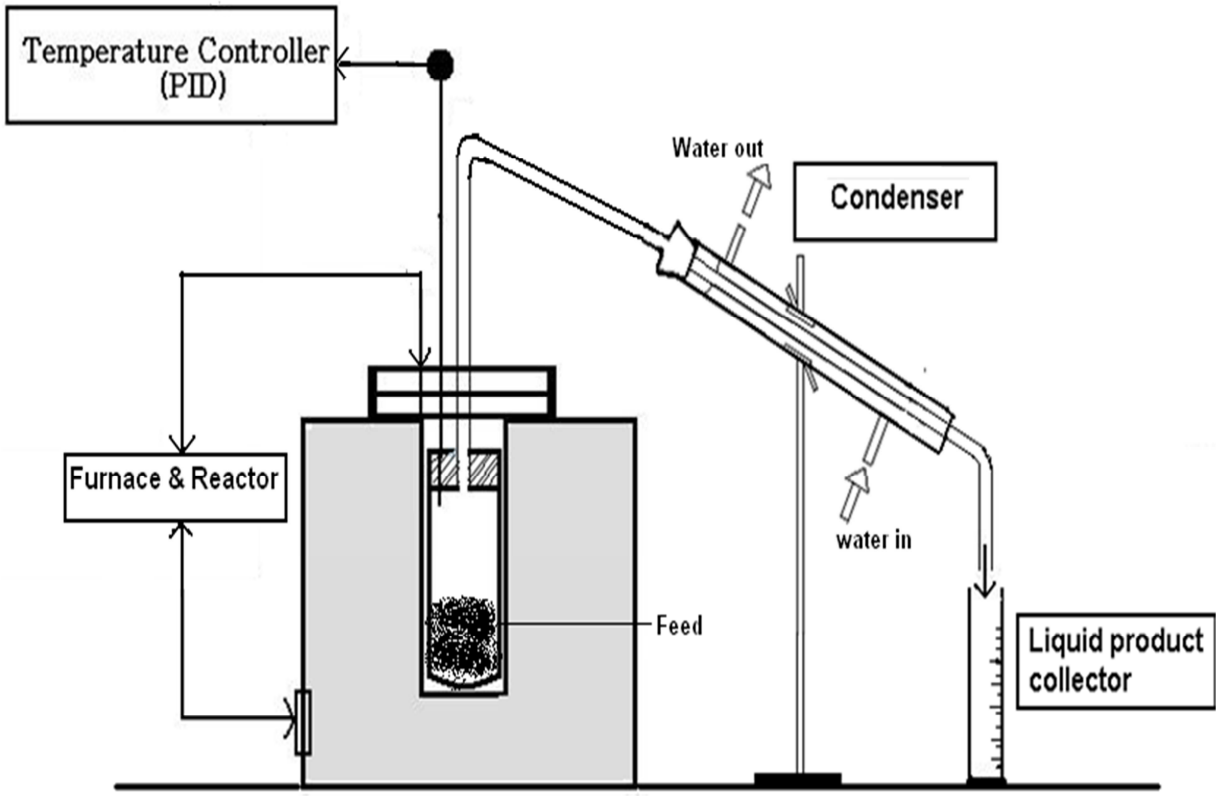

Fig .1The schematic diagram of experimental setup for pyrolysis.

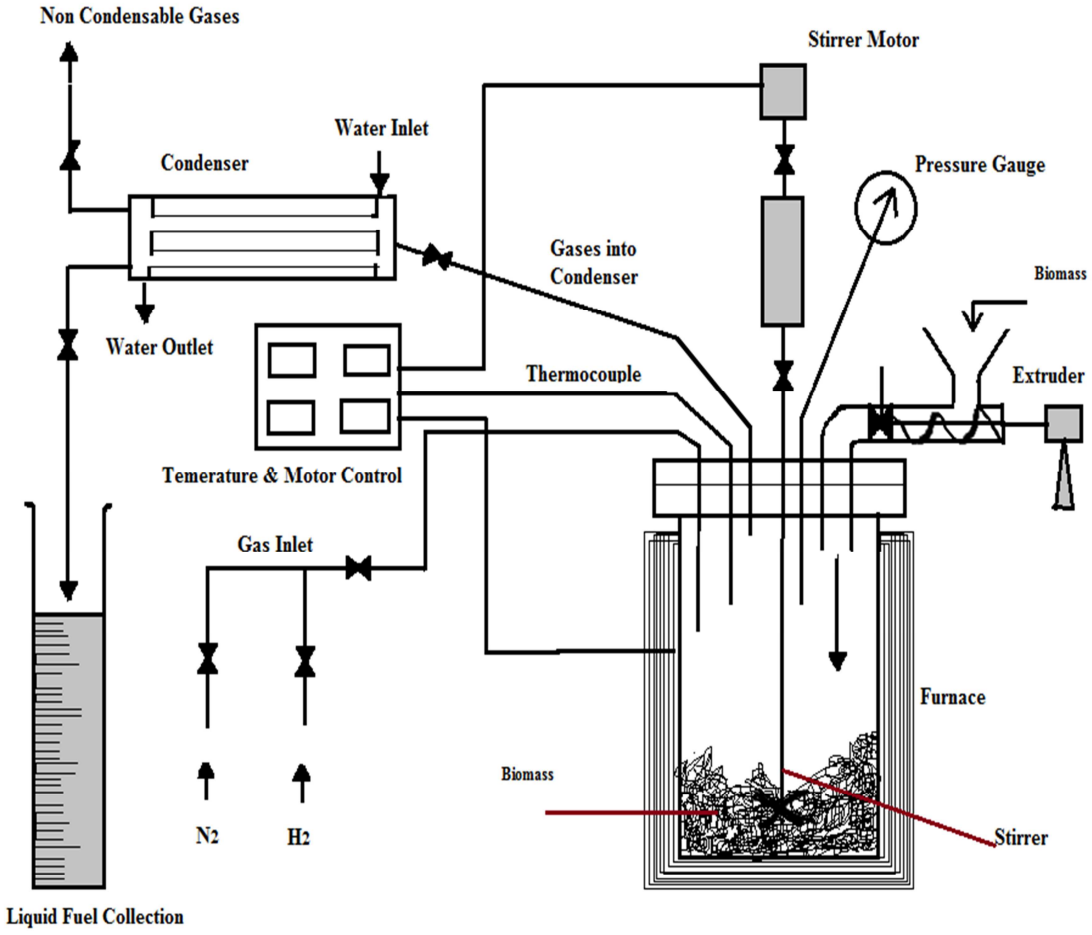

Fig.2 The schematic diagram of semi-batch reactor for pyrolysis (Shimaden FP93)

4.4. Sample Pyrolysis Runs

Once the temperature range was established then sample pyrolysis runs were done with 30gms of seeds (sesame and groundnut seed) in that range at intervals of 50°C to determine the temperature at which maximum yield of liquid product is obtained. It was heated externally by electric furnace at a heating rate of 25°C min^{-1} .The temperature of the furnace is maintained by a highly sensitive proportional-integral-derivative(PID) controller and the temperature is measured by Cr-Al:K type thermocouple fixed in the reactor. During sample runs various data like reaction time, yield of char, and yield of liquid product were noted down. Variation in yield of char, liquid product and gas (volatiles) with respect to temperature is plotted. Variation in reaction time with temperature was also plotted.

4.5 Characterization of the obtained liquid product

4.5.1 Physical Characterization of Bio-Oil

Physical properties such as density, specific gravity, viscosity, conradson carbon, flash point, fire point, pour point, cloud point, calorific value, sulphur content, distillation boiling range and cetane index of the bio-oil was determined using the standard methods.

4.5.2Chemical Characterization of Bio-Oil

4.5.2.1 FTIR

Fourier Transform Infrared spectroscopy (FTIR) is an important analysis technique that detects various characteristic functional groups available in oil. Interaction of an infrared light with oil the chemical bond will stretch, contract, and absorb infrared radiation in a specific wave length range in the presence of the rest of molecules. Based on this, the principle functional groups present in the pyrolytic oil were identified. The FTIR spectra were collected generally in the range of 400-4000 cm^{-1} region with $8cm^{-1}$ resolution.

Absorption in the infrared region makes changes in vibrational and rotational status of the molecules. The absorption frequency depends greatly on the vibrational frequency of the molecules. The absorption intensity depends on how the infrared photon energy can be transferred to the molecule. This depends on the change in the dipole moment that occurs as a result of molecular vibration. A molecule will absorb infrared light only if the absorption causes a change in the dipole moment. All compounds except for elemental diatomic gases such as N_2, H_2 and O_2, have infrared spectra and most components present in a flue gas is also analysed by their characteristic infrared absorption. If only one species is analysed, a species-specific instrument can also be used. Analysis is carried out in a narrow wavelength interval, where the species of interest has a characteristic absorption. Other components present in the sample also absorb at the analytical wavelength, so the spectrometer should be calibrated for cross

sensitivities. Quantification of several components absorbing in the mid infrared region (400-5000cm^{-1}), either conventional dispersive infrared analysis or Fourier Transform Infrared (FTIR) spectroscopy can also be used. Compared to dispersive IR analysis, FTIR analysis is faster and has a better signal to noise ratio.

In a FTIR instrument, the monochromator and the slits are replaced by an interferometer of Michelson type. A beam of radiation is divided into two beams by means of a beamsplitter. A path difference between the beams is also introduced whereupon it is allowed to recombine. In this way, interference between the beams is obtained. Intensity of the output beam from the interferometer is monitored as a function of path difference using an appropriate detector.

In order to determine the functional groups present in the pyrolytic oil, Fourier Transform Infrared spectroscopy of the oil was analyzed in a Perkin-Elmer infrared spectrometer.

4.5.2.2GC-MS

Gas Chromatography – Mass Spectrometry of the pyrolytic oil was performed using a GC-MS OP 2010[SHIMADZU] analyzer to determine the Chemical compounds present in the oil.

Chromatography is specially used to separate mixtures of chemicals into individual components for identification. After isolation, the components can be evaluated individually. In all most all chromatography, separation generally occurs when the sample mixture is introduced or injected into a mobile phase. In case of liquid chromatography, the mobile phase is a solvent. In the gas chromatography (GC), the mobile phase is an inert gas for example helium. Mobile phase carries the sample mixture through what is referred as stationary phase. The stationary phase is considered as a chemical that can also attract components in a sample mixture. This tube is called as a column. Columns can be glass or stainless steel of various dimensions. The mixture of compounds in the mobile phase interacts with the stationary phase. Each and every compound in a mixture interacts at a different rate. That interact the fastest will exit (elute from) the column first. Those that interact slowest will exit the column last. By observing the changing

characteristics of the mobile phase and the stationary phase the different mixtures of chemicals can be separated. Further refinements to this separation process are also made by changing the temperature of the stationary phase or the pressure of the mobile phase. GC has a long, thin column containing a thin interior coating of a solid stationary phase (5% phenyl-, 95% dimethylsiloxane polymer). This 0.25 mm diameter column is called as a capillary column. This particular column is used for semi volatile, non-polar organic compounds such as the PAHs we will look at. The capillary column is held in an oven that can be programmed to increase the temperature gradually (or in GC terms, ramped). As the temperature increases, that compounds which have low boiling points elute from the column sooner than those that have higher boiling points. There are actually two distinct temperature, separating forces and stationary phase interactions mentioned previously. After the compounds are separated, they just elute from the column and enter a detector. Detector is capable of creating an electronic signal whenever the presence of a compound is detected. Greater the concentration in the sample the bigger the signal becomes. The signal is then processed by the computer. Time from when the injection is made (time zero) to when elution occurs is referred to as the retention time (RT). While the instrument runs, the computer generally generates a graph from the signal. Each of the peaks in the chromatogram represents the signal created only when a compound elutes from the GC column into the detector. The x-axis shows the RT, and the y-axis shows the intensity (abundence) of the signal.

GC-MS is used both for the qualitative identification and for the quantitative measurement of volatile and semi volatile organic compounds in complex mixtures. The pyrolytic oil obtained was characterized by using GC/MS- QP 2010 SHIMADZU, equipped with the flame ionization and the mass spectrometry detection (GC-FID-MS). A capillary column coated with a 0.25 µm film of DB-5 with length of 30 m and diameter 0.25 mm was used. The GS was equipped with a split injector at 200ºC with a split ratio of 1:10. Helium gas of 99.995% purity was used as carrier gas at flow rate of 1.51 ml/min. The oven initial temperature was set to 70 ºC for 2 min and then increased to 300 ºC at a rate of 100 ºC/min and maintained for 7 min. All the compounds can be identified by means of the NIST library. Mass spectrometer was generally

operated at an interface temperature of 240ºC with ion source temperature of 200 ºC of range 40-1000 *m/z.*

Table.1.GC–MS conditions

Instrument	**GC–MS-OP 2010 [SHIMADZU]**	
GC conditions		
Column oven	70 °C temperature	
Injection temperature	200 °C	
Flow control mode	Linear velocity	
Column flow	1.51 ml/min	
Carrier gas	Helium 99.9995% purity	
Column oven temperature progress		
Rate	Temperature (°C)	Hold time (min)
–	70	2
10	300	7.0 (32 min total)
Column: DB-5		
Length	30.0 m	
Diameter	0.25 mm	
Film thickness	0.25 lm	
MS conditions		
Ion source temperature	200 °C	
Interface temperature	240 °C	
Start m/z	40	
End m/z	1000	

4.5.3 Characterization of char

4.5.3.1 1H- NMR:

Proton NMR also known as Hydrogen-1 NMR, or ^{1}H NMR is the application of nuclear magnetic resonance in NMR spectroscopy with respect to hydrogen-1 nuclei within the molecules of a substance. To determine the structure of its molecules in samples where natural hydrogen (H) is used, practically all of the hydrogen consists of the isotope ^{1}H (hydrogen-1is having a proton for a nucleus). A full ^{1}H atom is called protium. NMR spectra are recorded in the solution and solvent protons must not be allowed to interfere. Deuterated (deuterium = ^{2}H, often symbolized as D) solvents especially for use in NMR are preferred, such as deuterated chloroform ($CDCl_3$). However, a solvent without hydrogen such as carbon tetrachloride (CCl_4) or carbon disulphide (CS_2) may also be used. Deuterated solvents were usually supplied with a small amount of (typically 0.1 %) of tetramethylsilane (TMS) as an internal standard for calibrating the chemical shifts of each analyte proton. TMS is generally a tetrahedral molecule, with all the protons being chemically equivalent which gives one single signal, used to define a chemical shift = 0 ppm. It is volatile, making sample recovery easy as well. Modern spectrometers are also able to reference spectra based on the residual proton in the solvent (e.g. the $CHCl_3$, 0.01 % in 99.99 % $CDCl_3$). Deuterated solvents are now commonly supplied without TMS.

Deuterated solvents permit the use of deuterium frequency-field lock (also known as deuterium lock or field lock) to offset the effect of the natural drift of the NMR's magnetic field B_0. In order to provide the deuterium lock, the NMR monitors the deuterium signal resonance frequency from the solvent and makes changes to the B_0 to keep the resonance frequency constant. Additionally, the deuterium signal is used to accurately define 0 ppm as the resonant frequency of the lock solvent. The difference between the lock solvent and 0 ppm (TMS) are well known. Proton NMR spectra of the most organic compounds are characterized by chemical shifts in the range +14 to -4 ppm and by spin-spin coupling between protons. The integration curve for each of the proton reflects the abundance of the individual protons.

1H-NMR spectra were recorded by using a 400 MHz, BRUKER DPX-400, High performance digital FT–NMR spectrometer by using chloroform-d containing TMS (tetramethylsilane) as the internal standard.

4.5.3.2 SEM-EDX:

Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. EDX relies on the investigation of an interaction of some source of X-ray excitation and a sample. The characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum to stimulate the emission of characteristic X-rays from a specimen. High-energy beam of charged particles such as electrons or protons a beam of X-rays is focused into the sample is being studied. An atom within the sample contains ground state electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam excites an electron in an inner shell which ejects it from the shell while creating an electron hole where the electron was. An electron from a higher-energy shell then fills the hole. Difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. Number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. The energy of the X-rays are characteristic of the difference in energy between the two shells. The atomic structure of the element from which they were emitted allows the elemental composition of the specimen to be measured.
Scanning electron microscopy images were taken by using JEOL (JSM-6480 LV) microscope with an acceleration voltage of 15 kV

CHAPTER – 5

RESULTS AND DISCUSSION

5. RESULTS AND DISCUSSION:

5.1 Proximate analysis of the two raw materials:

Table.2.Proximate analysis and calorific value of sesame and groundnut seed

S.No	Property	Sesame seed (%)	Groundnut seed (%)
1	Moisture content	3.6	4.0
2	Volatile content	38.0	39.4
3	Ash content	6.0	2.1
4	Fixed carbon	52.4	54.5
5	C	55.71	58.56
6	H	8.48	9.14
7	N	4.03	4.60
8	S	0.34	0.38
9	O	31.42	27.28
10	C/H	0.54	0.53
11	C/N	8.05	7.41

12	C/O	2.36	2.86
13	% Oil Content	58.97	70.95
14	Empirical formula	$C_{1.61} H_{0.24} O_{0.90} N_{0.11} S_{0.01}$	$C_{0.11} H_{0.23} O_{0.70} N_{0.11} S_{0.01}$
15	Calorific value (kJ/kg)	29433.20	28198.09
16	Calorific value ((kJ/kg)) using Bomb Calorimeter	28679.58	27339.80

5.2. Thermo Gravimetric Analysis

TGA (Thermo Gravimetric Analysis) study helps us in determining the range of temperature of pyrolysis. A sharp bend in the curve shows the temperature at which the pyrolysis has to be started and the temperature at which the curve gets flat shows the end temperature of the pyrolysis. From fig (2) the range of pyrolysis was observed to be from 200 to 600 ^{0}C at 10^{0}C/min and 200 to 400 ^{0}C at 25 ^{0}Cfor sesame seed and from the range of pyrolysis was found to be (fig-5)200 to 600 ^{0}C at 10^{0}C/min and 200 to 400 ^{0}C at 25 ^{0}C for groundnut seed. In this case the First stage decomposition represents the evaporation of moisture contents; Second decomposition indicates the formation of volatiles. During the Third stage, the pyrolysis residue slowly decomposed, with the weight loss velocity becoming smaller and smaller and the residue ratio tends to be constant at the end the decomposition of hydrocarbon. A three stage weight loss is observed. Due to high decomposition rate per unit time, the rapid decomposition zone or Second stage of decomposition is treated as active pyrolytic zone. During the Second stage, the intermolecular associations and weaker chemical bonds are destroyed. The side aliphatic chains may be broken and some small gaseous molecules are produces because of the higher temperature. During the Third stage at higher temperature chemical bonds are broken and the parent molecular skeletons are destroyed. As a result, the larger molecule decomposes to smaller

molecules in the form of gas phase. Finally ash remains.

DTA (differential Thermal Analysis) is a technique in which the temperature difference between a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to the same controlled temperature programmed. The record is the differential thermal or DTA curve. The temperature difference (ΔT) should be plotted on the ordinate with endothermic reactions downwards and temperature or time on the abscissa increasing from left to right. In almost all the DTA plot first the reaction is endothermic than exothermic.

5.3 TGA &DTA analysis of all the two samples have been shown in the below:

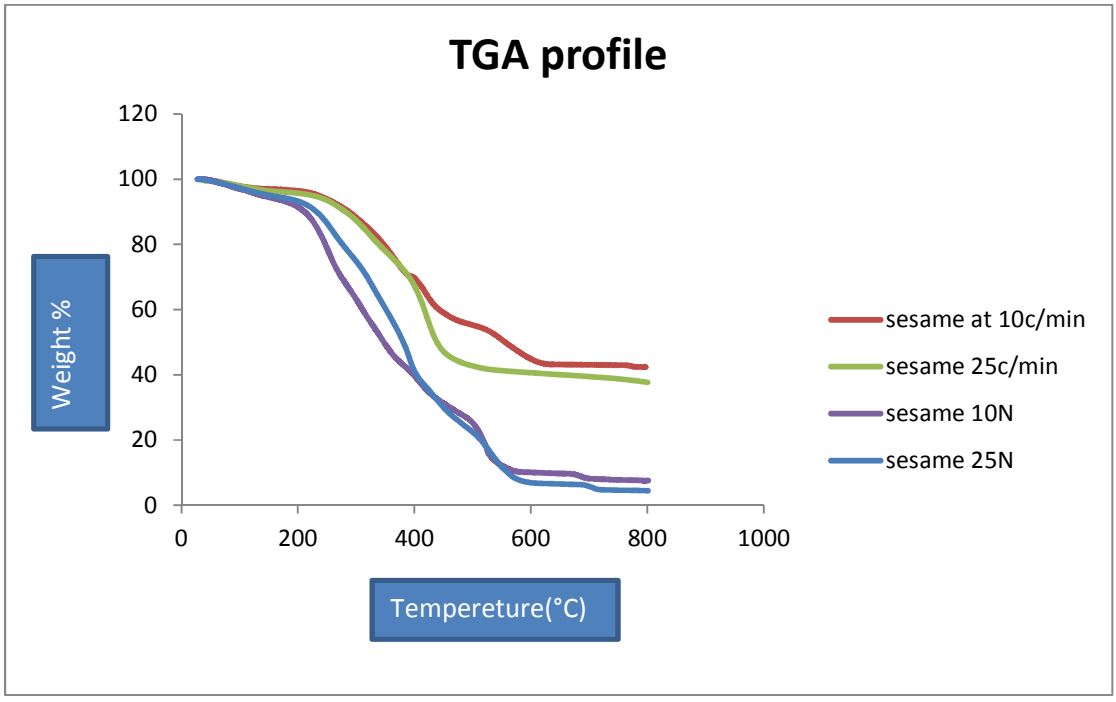

Fig.3 Comparison of TGA profile of sesame seed

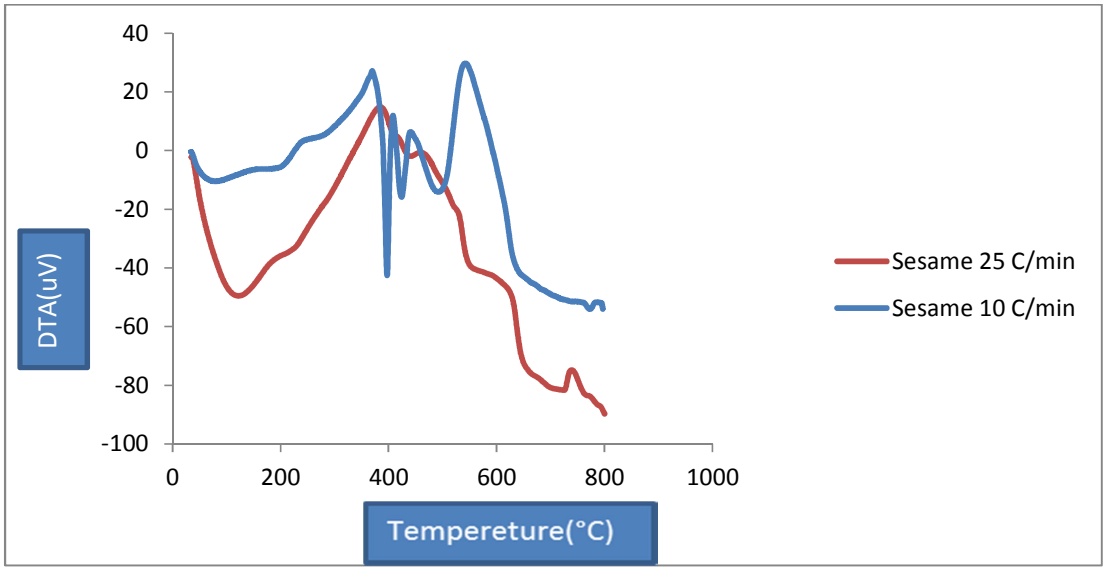

Fig.4 Comparison of DTA profile of sesame seed in air atmosphere

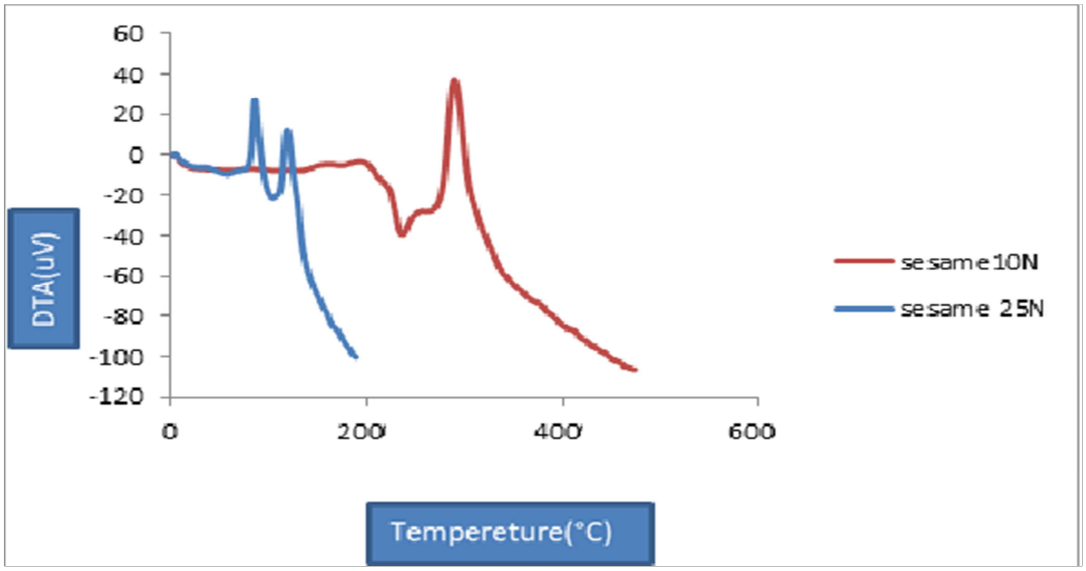

Fig.5Comparison of DTA profile of sesame seed in N_2 atmosphere

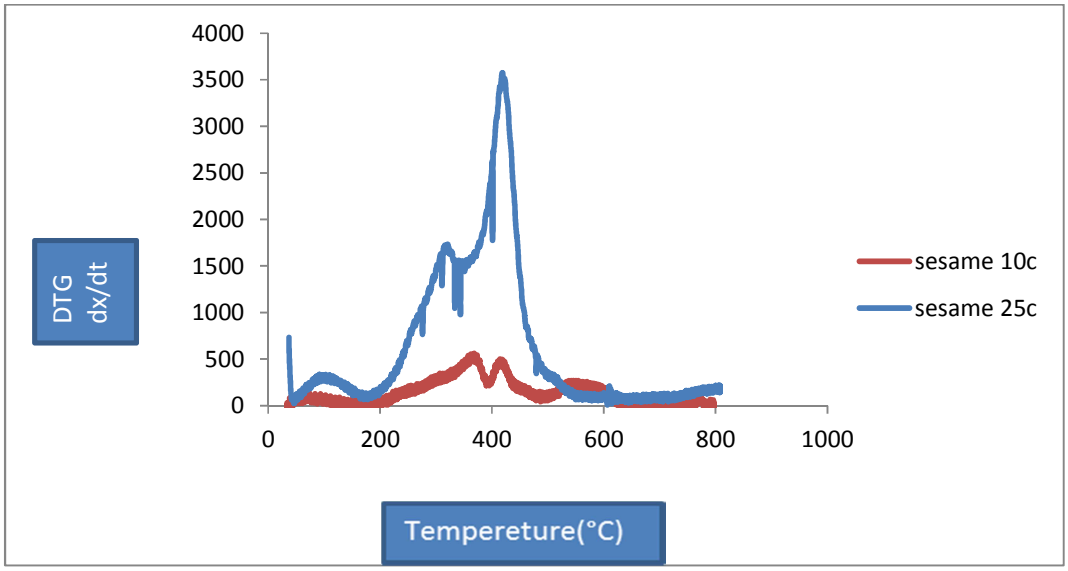

Fig.6 Comparison of DTG profile of sesame seed in air atmosphere

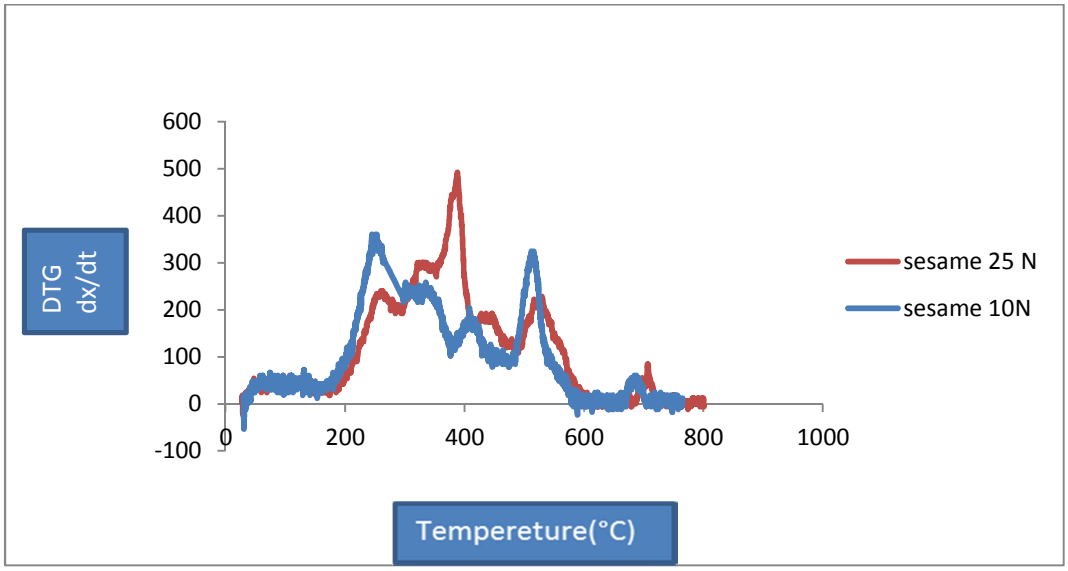

Fig.7 Comparison of DTG profile of sesame seed in N_2 atmosphere

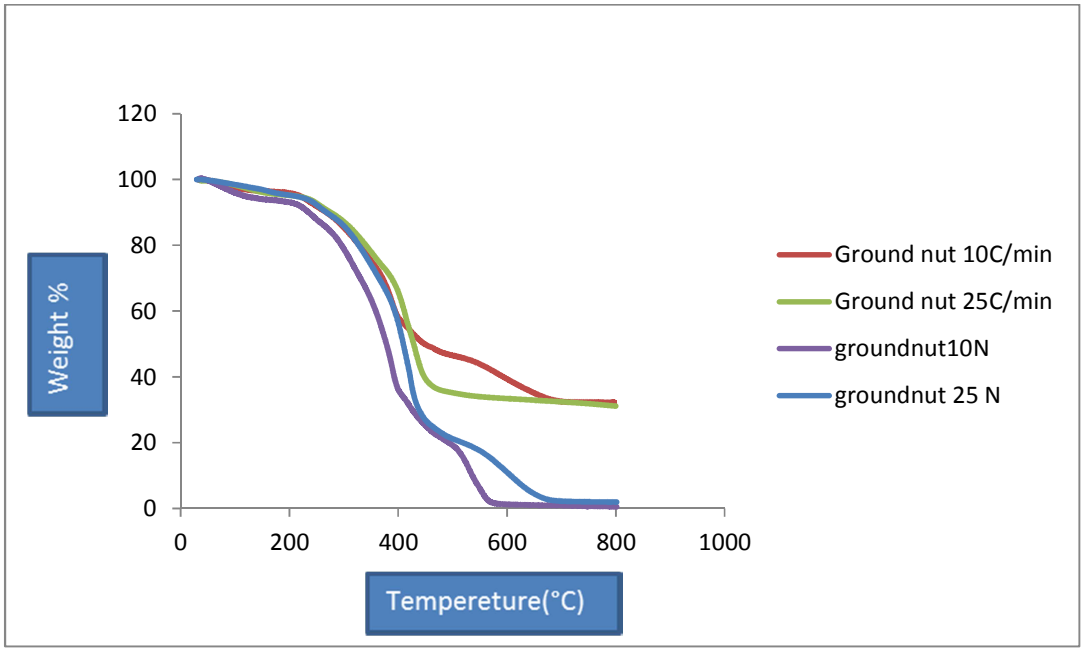

Fig.8 Comparison of TGA profile of groundnut seed

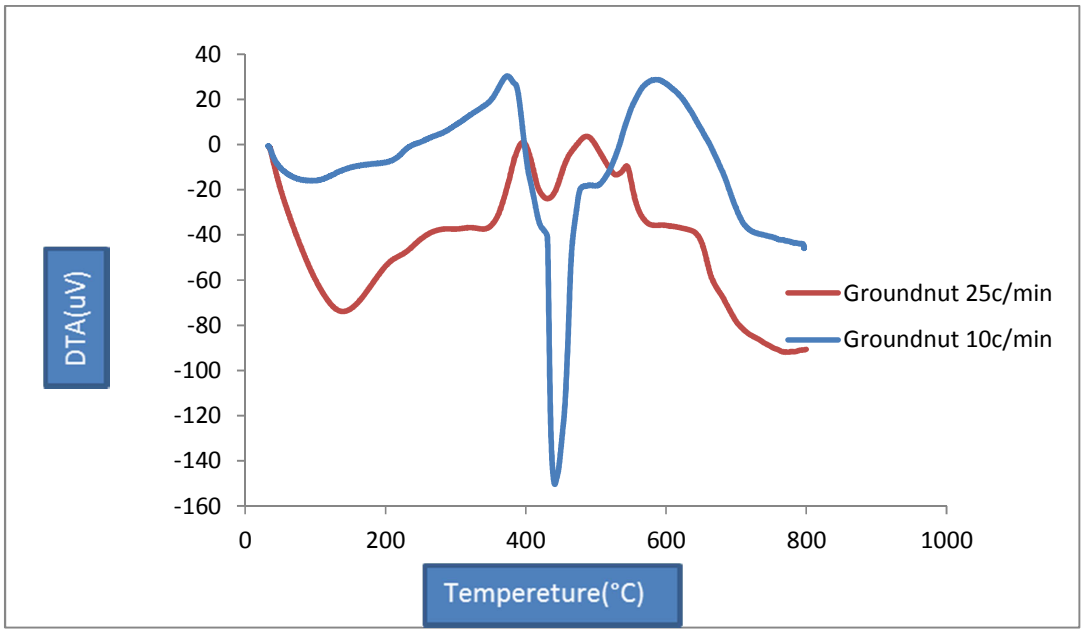

Fig.9Comparison of DTA profile groundnut seed in air atmosphere

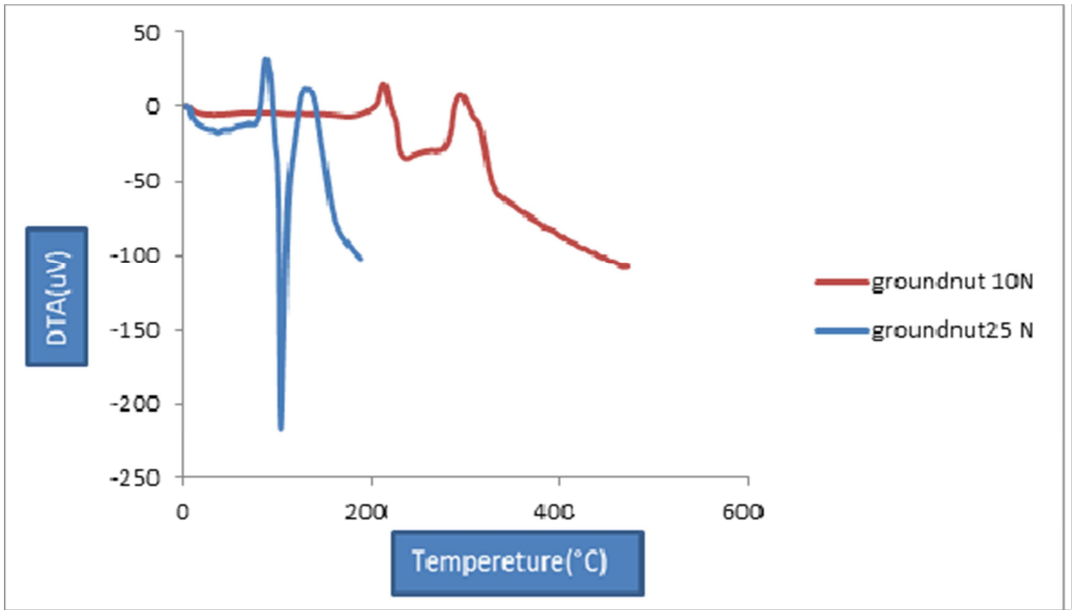

Fig.10Comparison of DTA profile groundnut seed in N_2 atmosphere

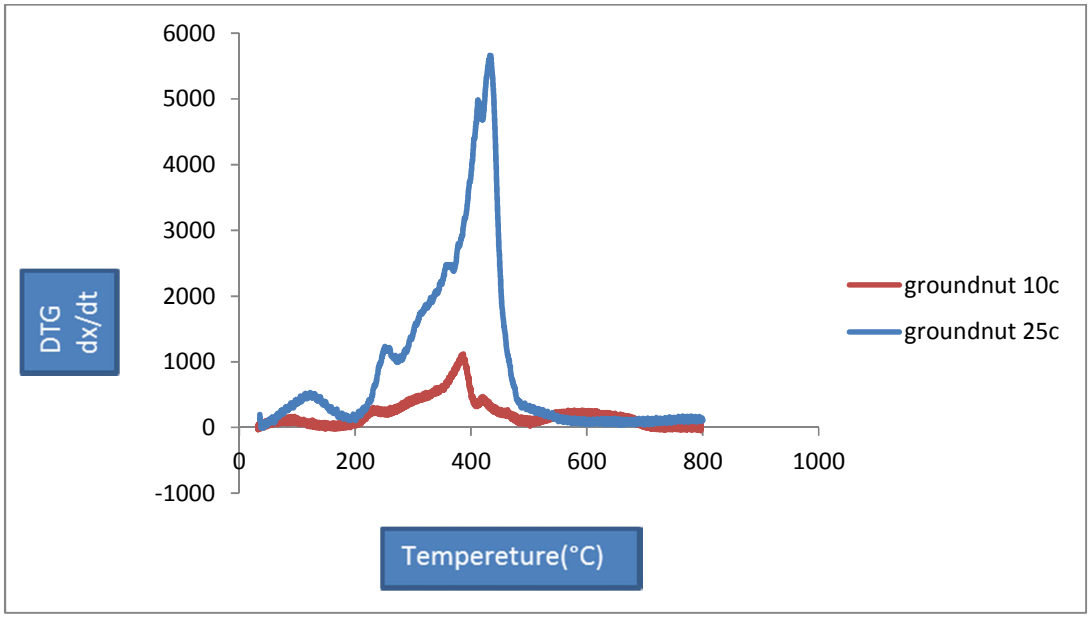

Fig.11Comparison of DTG profile groundnut seed in air atmosphere

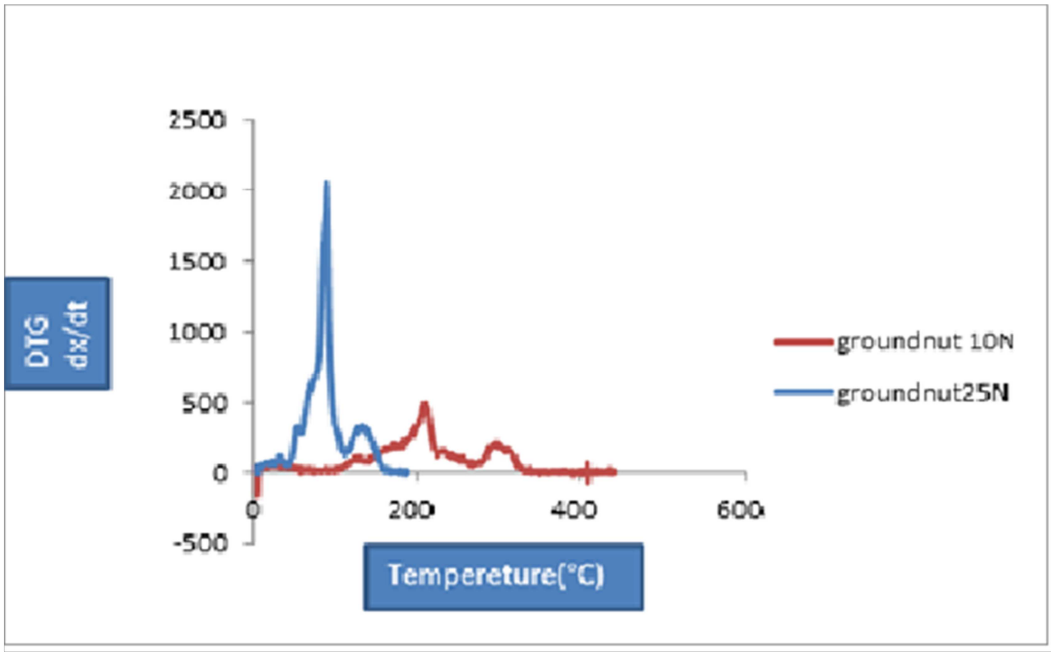

Fig.12Comparison of DTG profile groundnut seed in N_2 atmosphere

5.4 Experimental Results:

Table.3 experimental result of sesame seed

Temperature (^{0}C)	**Sesame seed**					
	400	**450**	**475**	**500**	**525**	**550**
Weight % of oil	15.25	25.65	46.54	58.97	52.32	47.86
Weight % of char	43.97	34.61	23.24	23.21	20.55	18.78
% Volatiles	40.77	39.72	30.21	17.81	27.12	33.35
Time of the reaction(min)	60	51	48	45	30	20

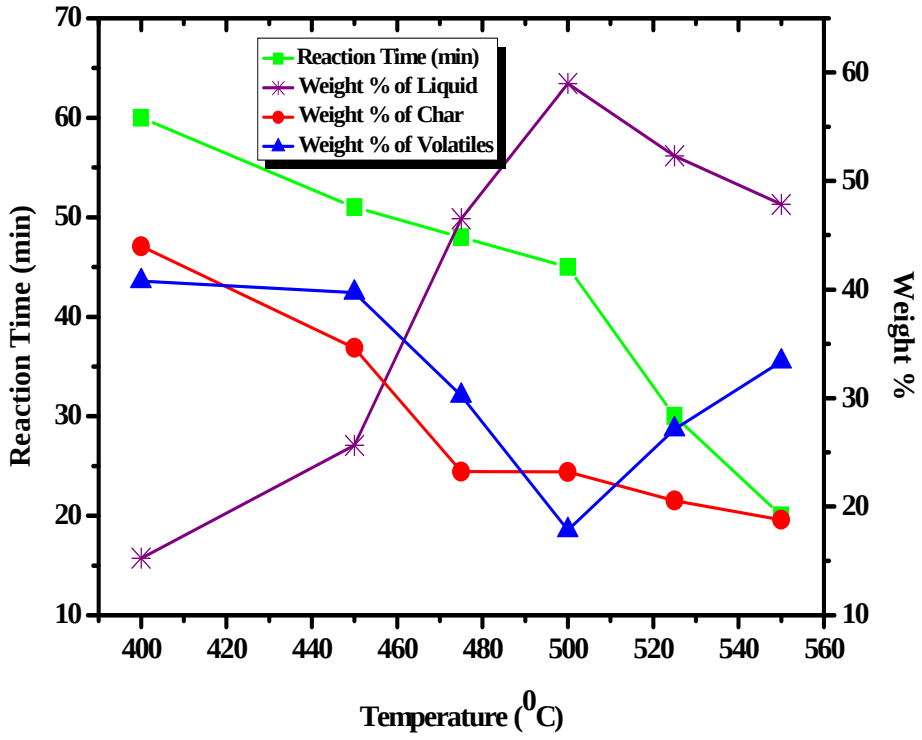

Figure.13. Product yields for the pyrolysis of sesame seed in relation to temperature

Table.4 experimental result of groundnut seed

Temperature (^{0}C)	**Groundnut seed**					
	400	**450**	**475**	**500**	**525**	**550**
Weight % of oil	27.69	62.95	65.80	70.95	54.96	47.16
Weight % of char	49.96	20.29	16.88	17.94	16.00	13.94
% Volatiles	22.33	16.74	17.31	11.10	29.03	38.89
Time of the reaction(min)	47	40	37	31	28	25

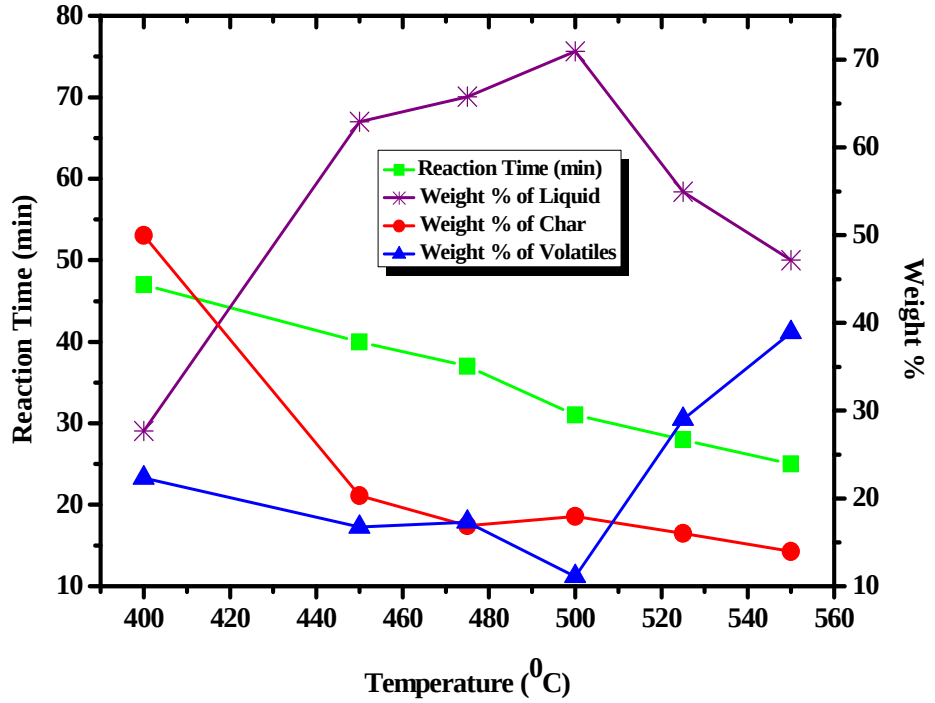

Figure.14. Product yields for the pyrolysis of groundnut seed in relation to temperature

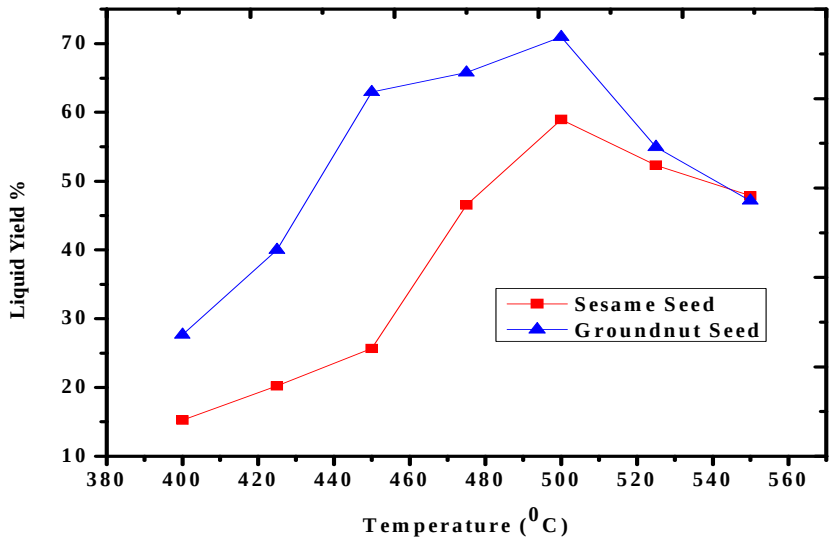

Figure 15 comparison of liquid product yields for oil seeds

From the above graphs it was observed that as the temperature is increased, the yield of liquid product increased, char yeald decreased. As the temperature is increased, volatile formation initally decreased upto 450-500ºC and then increased. From graphs it was observed that with increase in temperature, reaction time decreased.Liquid yield was highest at 500^0C in both the cases and having58.97 Wt. %, and 70.95Wt % of oil recovery respectively for sesame seed and groundnut seed. Maximum oil recovery was found in case of groundnut seed.

5.5. Characterization of Liquid Product:

5.5.1 FTIR of oil samples

Fourier Transform Infrared spectroscopy (FTIR) is an important analysis technique which detects various characteristic functional groups present in oil. On interaction of an infrared light with oil, chemical bond will stretch, contract, and absorb infrared radiation in a specific wave length range regardless structure of the rest of the molecules. Figure 16 and 17 shows the FTIR spectra of sesame and groundnut seed oil. The different assignments of the FTIR spectra of sesame and groundnut oil are summarized in table 5 and 6 which shows the presence of mostly alkane and alkenes. The results were found consistent when compared with the results of GC-MS.

Table 5 FTIR assignment of sesame seed oil obtained at 500^0C

Wave number (cm^{-1})	**Type of vibration**	**Nature of functional group**
2852	C-H stretching	Alkane
2922	C-H stretching	Alkane
2091	C≡C stretching	Alkyne
1644	C=C stretching	Alkene

1553	C=C stretching	Aromatic rings
1413	C-H Scissoring and bending	Alkene
575.01	NO_2 bending	Nitro compound

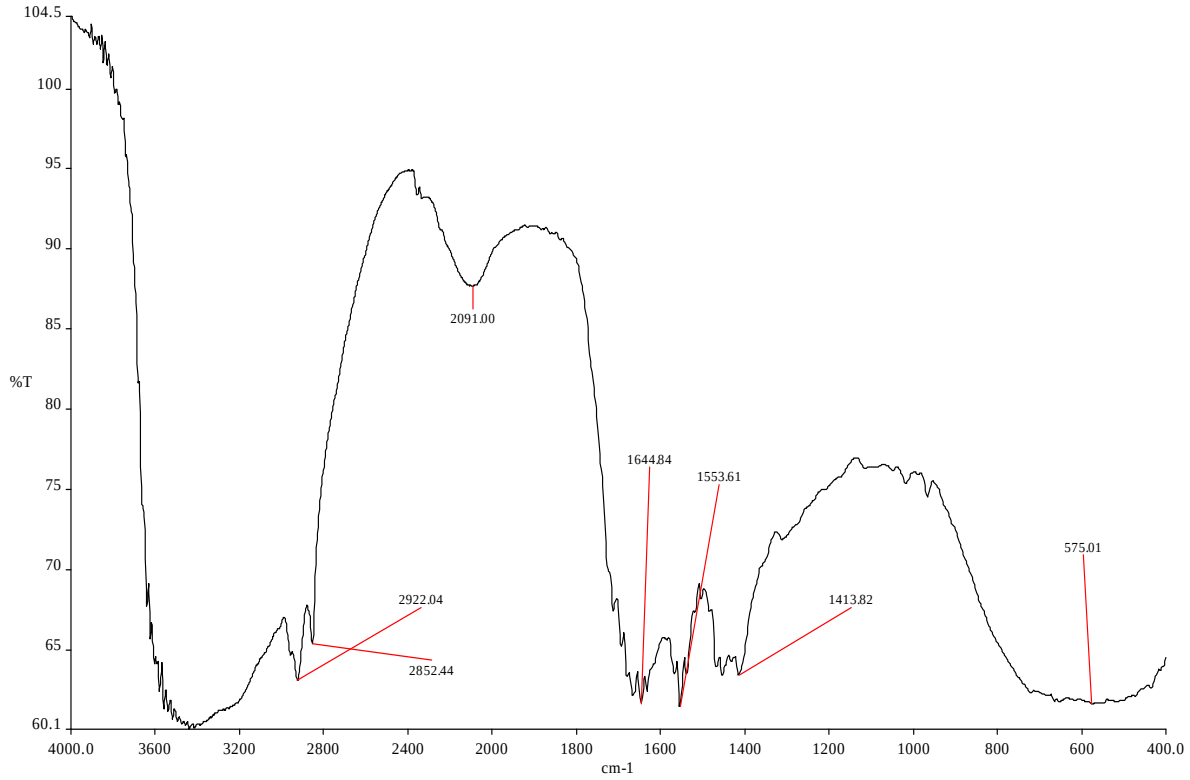

Figure 16- FTIR spectrometry of sesame seed oil obtained at 500^0C

Table 6 FTIR assignment of groundnut seed oil obtained at 500^0C

Wave number (cm^{-1})	Type of vibration	Nature of functional group
3650	O-H (free) usually sharp	Alcohols and Phenols
3630	O-H (free) usually sharp	Alcohols and Phenols
3617	O-H (free) usually sharp	Alcohols and Phenols
3075	C−H (m) stretching	Aromatic rings
2955	C−H (m) stretching	Alkanes
2923	C−H stretching	Alkanes
2853	C−H (med)	Aldehyde group
2360	P−H	Phosphine group
2341	P−H	Phosphine group
1702	C−H fingerprint region	Phenyl ring substitution overtones
1640	C═C stretching	Alkenes
1463	C−H scissoring and bending	Alkanes
1376	C−H scissoring and bending	Alkanes

1302	C−N stretching	Amines
991	C-H bending	Alkenes
964	C-H bending	Alkenes
908	C-H bending	Alkenes
721	O−H bending	Phenyl ring substitution bands

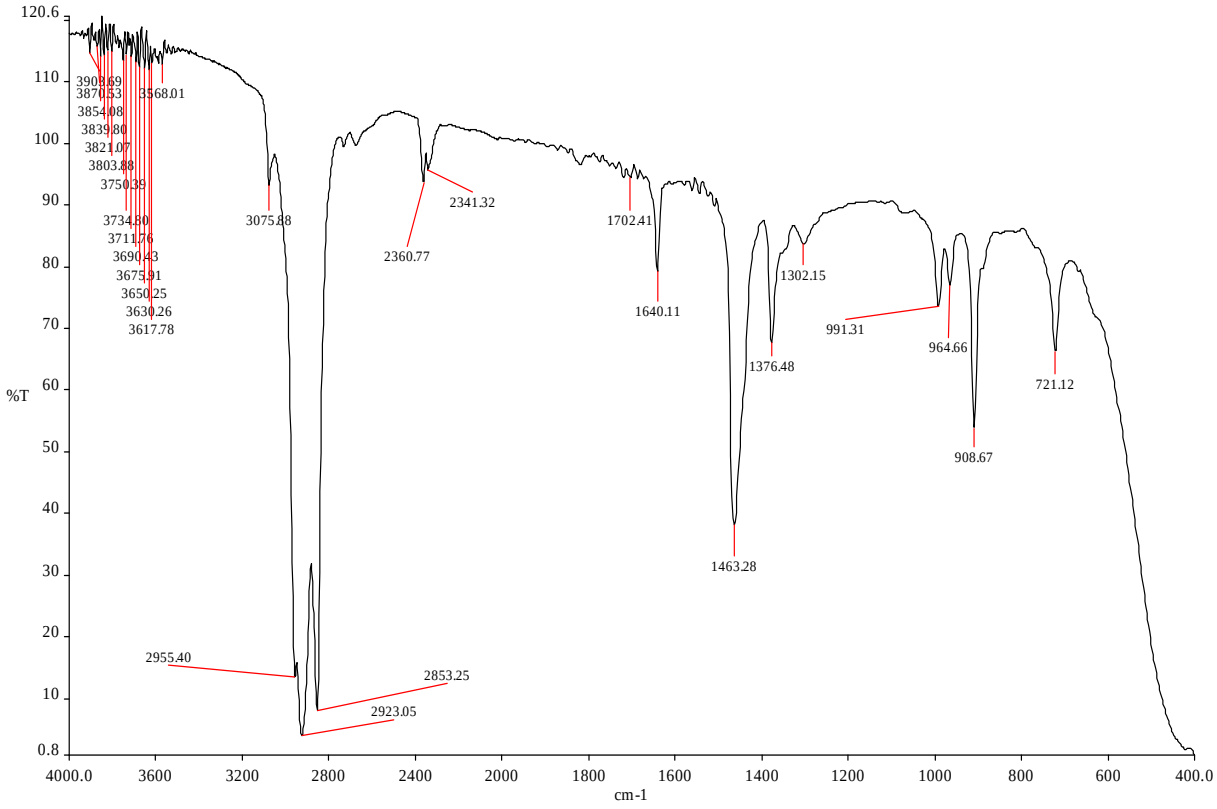

Figure-17.FTIR spectrometry of groundnut seed oil obtained at 500°C

5.5.2. GC-MS of oil samples

The GC-MS analysis of the oil sample obtained from oil seeds was carried out to know the exact composition of the oil (Figure 18 and 19) and is summarized in the Table 7 and 8. The components present in oil seed is mostly the aliphatic hydrocarbons (alkane and alkenes) with carbon no C_5-$C_{22.}$

The compounds mostly present in sesame seed pyrolytic oil are oleanitrile,9-octadecenamide, (3E)-3-Hexadecene nitrile, Hexadecanamide, 3-Heptadecene, (Z)-and Phenol. Oleanitrile is type of fatty acid generally present in bio-oil. 9-Octadecenamide is the amide of oleic acid and it has a great medicinal value. 9-Octadecenamide was first identified in the cerebrospinal fluid of sleep-deprived cats. 9-Octadecenamide has also been detected in the cerebrospinal fluid of rats and humans. 9-Octadecenamide induces physiological sleep when injected into rats. (3E)-3-Hexadecene nitrile is generally used in wide range of household, craft, and industrial products. Hexadecanamide can be used to produce palmitic acid-(2-amino-ethyl ester). 3-Heptadecene, (Z) has anti-tumor and anti-microbial activity. Phenol is mainly used in plastic industry.

The compounds mostly present in groundnut seed pyrolytic oil are Oleanitrile, Heptadecanenitrile, 3-Heptadecene, (Z)-, Oleyl amide, Nonadecane nitrile, n-Heptadecane, Pentadecane and Hexadecanamide. Oleanitrile is type of fatty acid generally present in bio-oil. Heptadecane is an organic compound which is an alkane hydrocarbon. Heptadecane is not suitable with strong oxidizing agents like nitric acid. 3-Heptadecene, (Z) has anti-tumor and anti-microbial activity.microbial activity. Oleyl amide is commonly used as organic intermediates and fabric assistant agent. Nonadecane nitrile is a saturated aliphatic hydrocarbon. It is used mainly in laboratories for research purpose. n-Heptadecane is an alkane hydrocarbon. Pentadecane is used as a perfuming agent. Hexadecanamide can be used to produce palmitic acid-(2-amino-ethyl ester).

Table-7 GC-MS Analysis of sesame seed pyrolytic oil

R.Time	Area%	Name of compound	Molecular formula
3.824	0.89	2-Furanmethanol	$C_5H_6O_2$
6.462	2.53	Phenol	C_6H_6O
8.125	2.51	4-Methylphenol	C_7H_8O
9.597	1.00	p-Ethylphenol	$C_8H_{10}O$
11.524	1.41	Indole	C_8H_7N
12.602	0.77	1-Pentadecene	$C_{15}H_{30}$
12.699	0.83	Tetradecane	$C_{14}H_{30}$
13.984	2.69	Pentadecane	$C_{15}H_{32}$
15.116	0.88	1-Hexadecene	$C_{16}H_{32}$
15.194	1.08	n-Hexadecane	$C_{16}H_{34}$
16.096	4.61	3-Heptadecene, (Z)-	$C_{17}H_{34}$
16.160	3.58	3-Heptadecene, (Z)-	$C_{17}H_{34}$
16.342	2.44	n-Heptadecane	$C_{17}H_{34}$
18.467	1.01	Pentacosane	$C_{25}H_{52}$
18.552	7.62	Heptadecanenitrile	$C_{17}H_{33}N$
20.258	4.26	9-Octadecynenitrile	$C_{18}H_{31}N$
20.314	19.77	Oleanitrile	C_2H_3N

20.353	8.33	(3E)-3-Hexadecene nitrile	C_{16} H_{29} N
20.536	3.36	Heptadecanenitrile	C_{17} H $_{33}$N
21.118	1.24	9-Octadecynenitrile	C $_{18}$H $_{31}$N
21.269	5.60	Hexadecanamide	C $_{16}$H$_{33}$ N O
21.788	1.32	Dodecane, 1-cyclopentyl-4-(3-cyclopentylpropyl)-	C_{25} H_{48}
22.349	1.27	Nonadecanenitrile	C_{19} H_{37} N
22.826	18.57	9-Octadecenamide, (Z)-	C_{18} H $_{35}$N O
24.015	2.44	Nonadecanenitrile	C $_{19}$H $_{37}$N

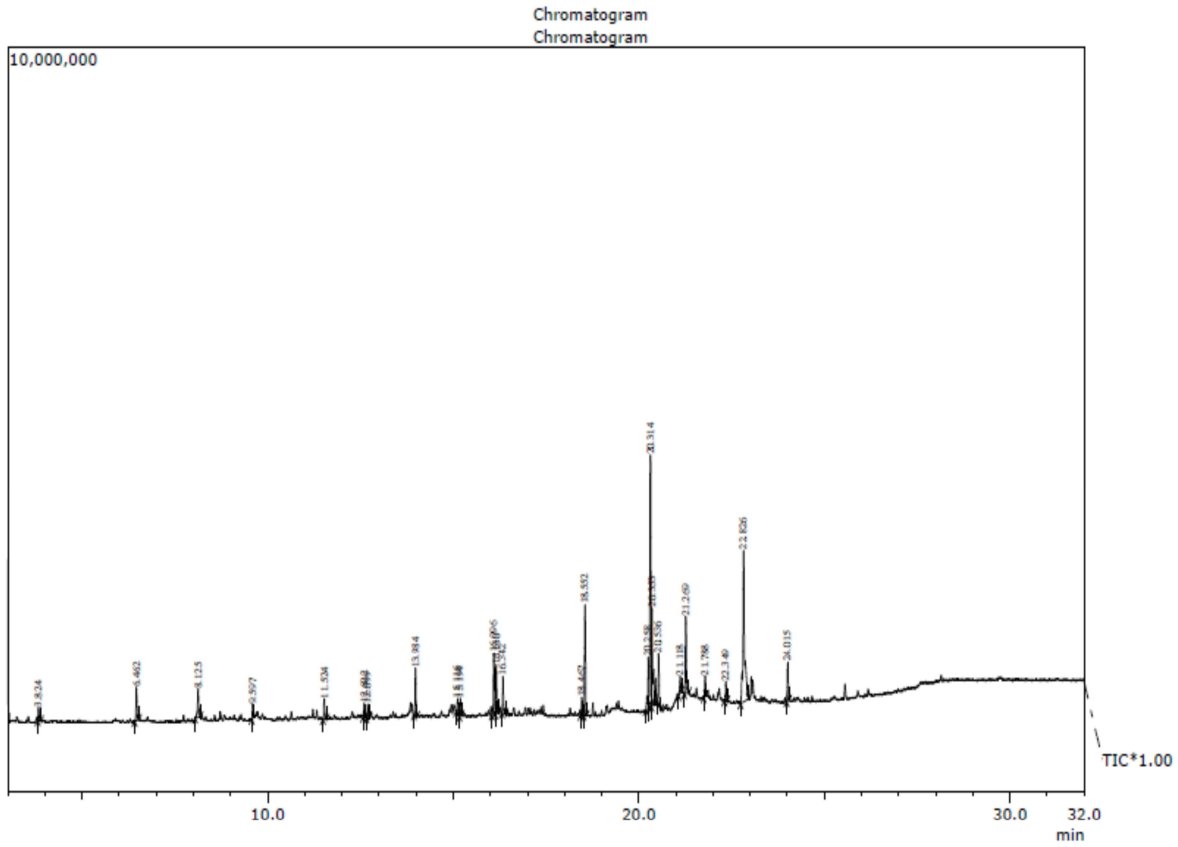

Figure 18- GC chromatogram of sesame seed oil obtained at 500^0C

Table-8.GC-MS Analysis of groundnut seed pyrolytic oil

R.Time	Area%	Name of compound	Molecular formula
6.462	1.01	Phenol	C_6H_6O
8.117	1.66	P-Cresol	C_7H_8O
11.217	0.53	1-Tridecene	$C_{13}H_{26}$
11.326	0.64	Tridecane	$C_{13}H_{28}$
12.601	0.74	1-Tetradecene	$C_{14}H_{28}$

12.697	1.27	Tetradecane	$C_{14}H_{30}$
13.894	0.49	1-Hexadecene	$C_{16}H_{32}$
13.983	4.52	Pentadecane	$C_{15}H_{32}$
14.956	0.73	9-Eicosene, (E)-	$C_{20}H_{40}$
15.017	0.87	1-Hexadecene	$C_{16}H_{32}$
15.114	0.93	1-Hexadecene	$C_{16}H_{32}$
15.193	1.63	Eicosane	$C_{20}H_{42}$
16.096	6.20	3-Heptadecene, (Z)-	$C_{17}H_{34}$
16.161	6.58	3-Heptadecene, (Z)-	$C_{17}H_{34}$
16.342	4.55	n-Heptadecane	$C_{17}H_{36}$
18.468	1.45	Nonadecane	$C_{19}H_{40}$
18.556	10.63	Heptadecanenitrile	$C_{17}H_{33}N$
20.261	2.89	9-Octadecynenitrile	$C_{18}H_{31}N$
20.318	18.14	Oleanitrile	$C_{18}H_{33}N$
20.358	9.81	Oleanitrile	$C_{18}H_{33}N$
20.400	2.91	n-Heneicosane	$C_{21}H_{44}$
20.540	5.99	Heptadecanenitrile	$C_{17}H_{33}N$
21.119	1.02	9-Octadecynenitrile	$C_{18}H_{31}N$
21.273	2.13	Hexadecanamide	$C_{16}H_{33}N$
21.557	0.49	N-Methylhexadecanamide	$C_{17}H_{35}NO$
22.172	1.55	Tetratetracontane	$C_{44}H_{90}$
22.349	1.47	Nonadecanenitrile	$C_{19}H_{37}N$
22.825	4.75	Oleyl amide	$C_{18}H_{35}NO$

24.016	2.62	Nonadecanenitrile	C_{19} H_{37} N
25.559	0.95	Nonadecanenitrile	C_{19} H_{37} N

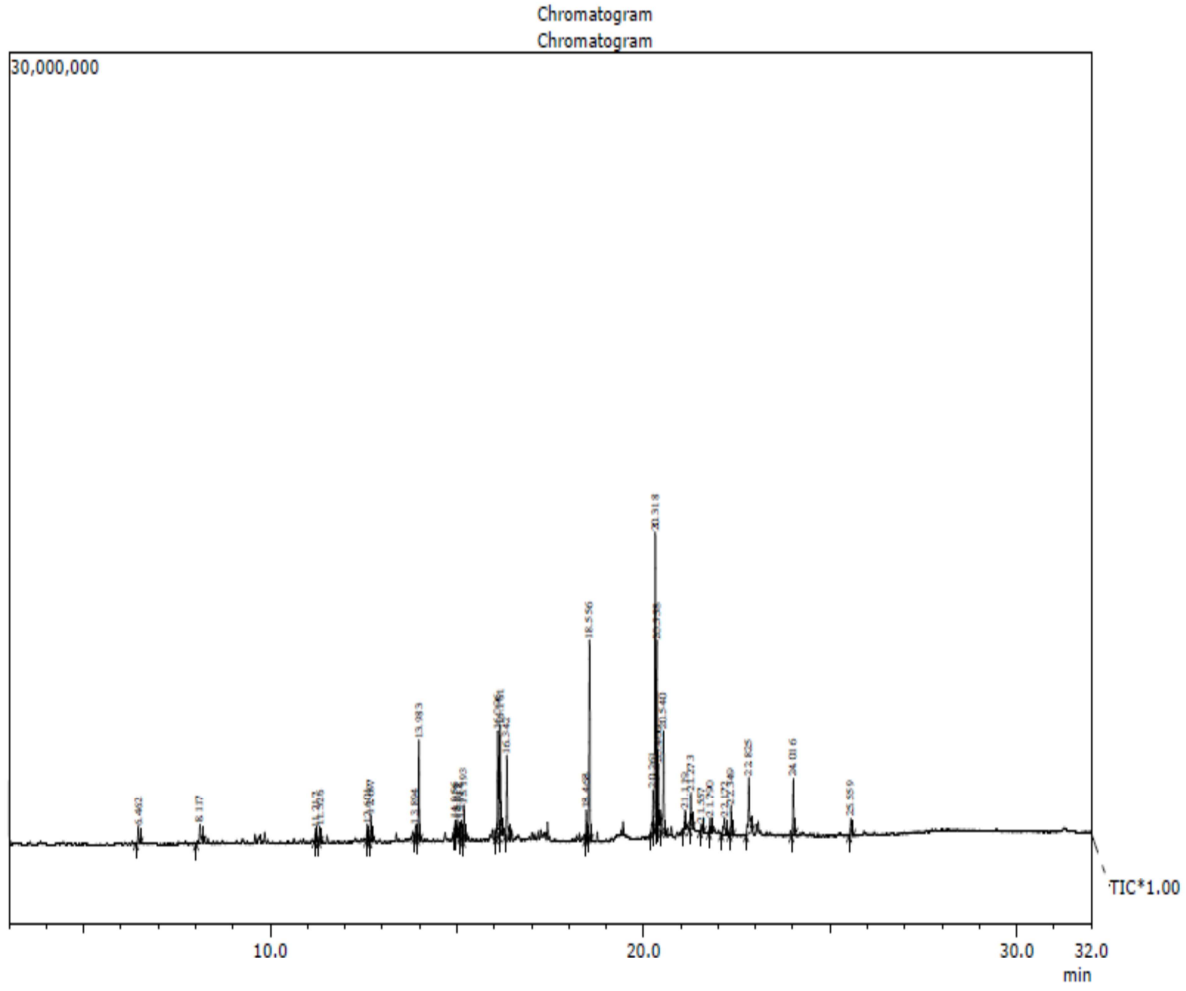

Figure 19- GC chromatogram of groundnut seed oil obtained at 500^0C

5.5.3. NMR analysis:

1H- NMR spectra were recorded by using a 400 MHz, Bruker DPX-400, High performance digital FT–NMR spectrometer was done by using chloroform-d containing TMS (tetramethylsilane) as the internal standard.

1H-NMR band assignments corresponding to structural features of sesame and groundnut pyrolytic oil is given in Table 9. β- CH_3, CH_2hydrogens attached to an aromatic ring were present in higher proportion in bio-oil and that accounts to 28.96 % for sesame seed bio-oil, 35.53% for groundnut seed bio-oil. About 3.61% of hydrogen was attached to hydroxyl groups or ring-join methylene in sesame seed bio-oil, 5.50% in groundnut seed bio-oil. CH_2 and CH_β to an aromatic ring (naphthenic) and CH_3 γ or further from an aromatic ring were also present. Hydrogen attached to phenolic (OH) or olefinic were also present up to 3.92% in sesame seed bio-oil, and 2.29% in groundnut seed bio-oil. But hydrogen attached to aromatics or conjugated olefins were not present and the spectrum are given in Figure. 20 and 21.

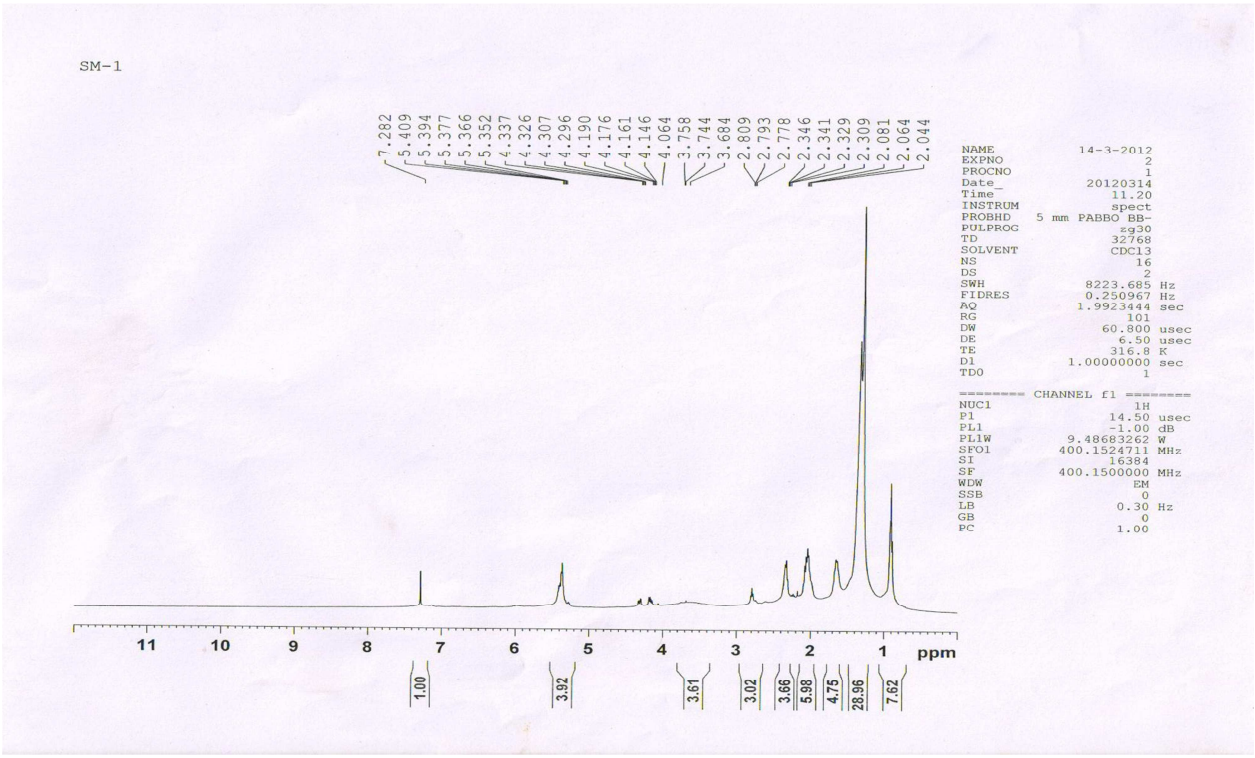

Figure. 20 1H-NMR spectrum of sesame seed pyrolytic oil.

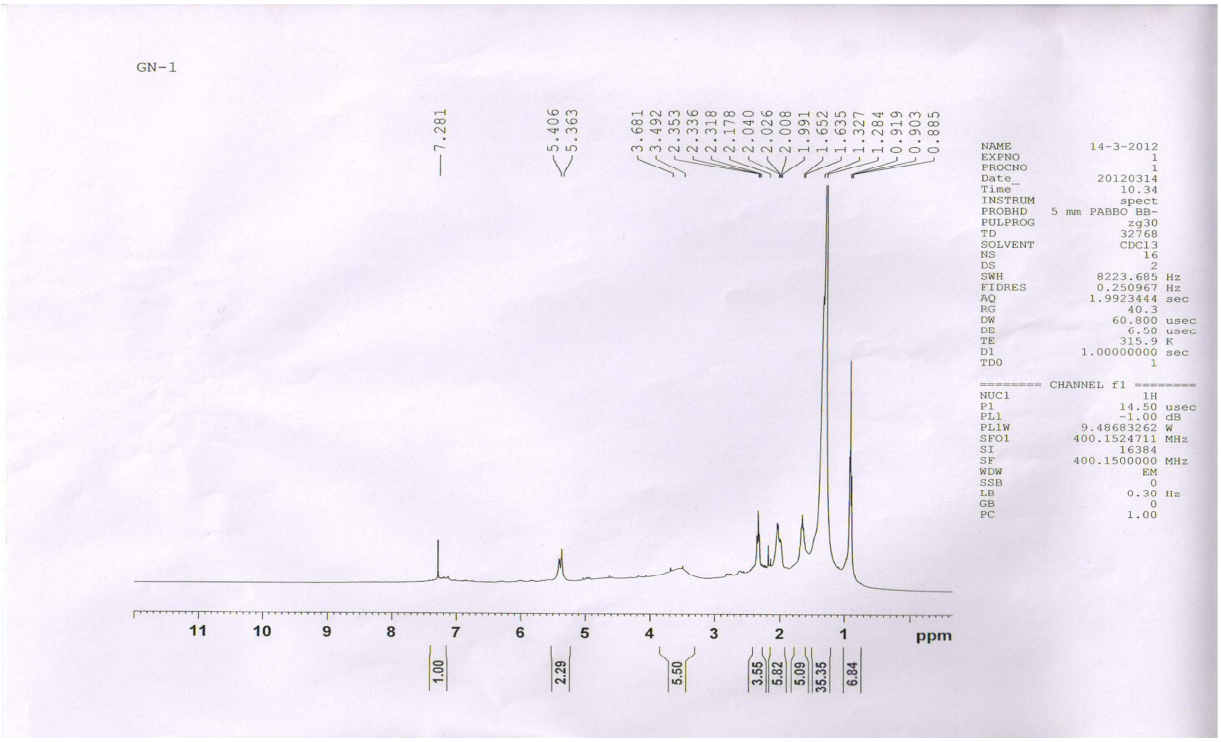

Figure.21 1H-NMR spectrum of groundnut seed pyrolytic oil.

Table 9 1H -NMR results of sesame and groundnut seedpyrolytic oil

Type of hydrogen	Chemical shift (ppm)	Percentage of Total Hydrogen (%)	
		Sesame seed	Groundnut seed
Phenolic (OH) or olefinic proton	6.5– 5.0	3.92	2.29
Hydroxyl groups or ring-join methylene(Ar–CH2–Ar)	4.5– 3.3	3.61	5.50
CH3 CH2 and CH to an aromatic ring	3.3– 2.0	12.66	9.37

CH2 and CH β to an aromatic ring (naphthenic)	**2.0– 1.6**	**4.75**	**5.09**
β-CH3, CH2 and CH γ to an aromatic ring	**1.6– 1.0**	**28.96**	**35.35**
CH3 γ or further from an aromatic ring	**1.0– 0.5**	**7.62**	**6.84**

5.5.4. Physical properties

Physical properties of sesame seed pyrolytic oil were found out by standard test methods:

Table-10Physical properties of sesame seed pyrolytic oil:

Tests	Results Obtained	Test method
Specific Gravity @ 15°C/15°C	0.9376	IS:1448 P:16
Density @ 15°C in kg/cc	0.9368	IS:1448 P:16
Kinematic Viscosity @ 40°C in Cst	48.9	IS:1448 P:25
Kinematic Viscosity @ 100°C in Cst	7.4	IS:1448 P:25
Viscosity Index	Plus 112	IS:1448 P:56
Conradson Carbon Residue	2.83%	IS:1448 P:122
Flash Point by Abel Method	48°C	IS:1448 P:20
Fire Point	56°C	IS:1448 P:20
Cloud Point	NA	IS:1448 P:10
Pour Point	Minus 2°C	IS:1448 P:10
Gross Calorific Value in Kcal/Kg	7237	IS:1448 P:6
Sulphur Content	0.43%	IS:1448 P:33

Calculated Cetane Index (CCI)	28.0	IS:1448 P:9
Distillation:		IS:1448 P:18
Initial Boiling Point	88°C	
Final Boiling Point	349°C	

Physical properties of groundnut seed pyrolytic oil were found out by standard test methods:

Table-11Physical properties of groundnut seed pyrolytic oil:

Tests	Results Obtained	Test method
Specific Gravity @ 15°C/15°C	0.9619	IS:1448 P:16
Density @ 15°C in kg/cc	0.9611	IS:1448 P:16
Kinematic Viscosity @ 40°C in Cst	4.71	IS:1448 P:25
Kinematic Viscosity @ 100°C in Cst	NA	IS:1448 P:25
Viscosity Index	NA	IS:1448 P:56
Conradson Carbon Residue	1.21%	IS:1448 P:122
Flash Point by Abel Method	46°C	IS:1448 P:20
Fire Point	55°C	IS:1448 P:20
Cloud Point	7ºC	IS:1448 P:10
Pour Point	Minus 2°C	IS:1448 P:10
Gross Calorific Value in Kcal/Kg	6497	IS:1448 P:6
Sulphur Content	0.05%	IS:1448 P:33
Calculated Cetane Index (CCI)	23.0	IS:1448 P:9

Distillation:		IS:1448 P:18
Initial Boiling Point	88°C	
Final Boiling Point	338°C	

5.6. Characterization of char:

5.6.1 PROXIMATE AND ULTIMATE ANALYSIS OF CHAR

Proximate and ultimate analysis of sesame seed char and groundnut seed char was done to determine the presence of volatile matter and characterized for its elemental composition by CHNS analysis and are tabulated in Table.10. Its Empherical formula, calorific value was also determined. It was found that even after pyrolysis still some volatile matter was present in the char. This shows that pyrolysis is not done completely. Carbon content was found to be almost same in all the char.

Table.12 Proximate and ultimate analysis of sesame seed char and groundnut seed char

S.No	Property	Sesame seed (%)	Groundnut seed (%)
1	Moisture content	1.83	2.44
2	Volatile content	3.71	5.50
3	Ash content	10	10

4	Fixed carbon	84.49	82.06
5	C	58.00	67.62
6	H	3.29	2.79
7	N	5.38	8.03
8	S	0.17	0.18
9	O	33.14	21.36
10	C/H	1.46	2.01
11	C/N	6.28	4.91
12	C/O	2.33	4.22
13	% Oil Content	NIL	NIL
14	Empirical formula	$C_{3.29}H_{0.18}O_{1.88}N_{0.30}S_{0.01}$	$C_{0.43}H_{0.15}O_{1.14}N_{0.43}S_{0.01}$
15	Calorific value (kJ/kg)	6336.75	6154.5

5.6.2. SEM ANALYSIS:

SEM-EDX is not only used for high magnification imaging but also for making a quantitative chemical analysis of unknown materials. The SEM can automatically perform analysis down to a particle size of 2 µm with the advantage of chemical characterization using EDX. With SEM in combination of EDX it is also possible to find out elemental composition of materials.-Scanning electron microscopy images were taken by using JEOL (JSM-6480 LV) microscope having an acceleration voltage of 15 kV, equipped with a 6587 EDX scanning spectrometry detector.

SEM analysis was done to find the surface morphology of char and are shown in Figure (22, 23, 24, 25). Figure (22, 23) are of sesame char taken at 1000X and 2000X magnification. Figure (24, 25) are of groundnut char taken at 1000X and 2500X magnification. These images showed heterogeneous distribution of pores and rough texture. The average pore sizes present on the char surface of the char was found to be 5 µm.

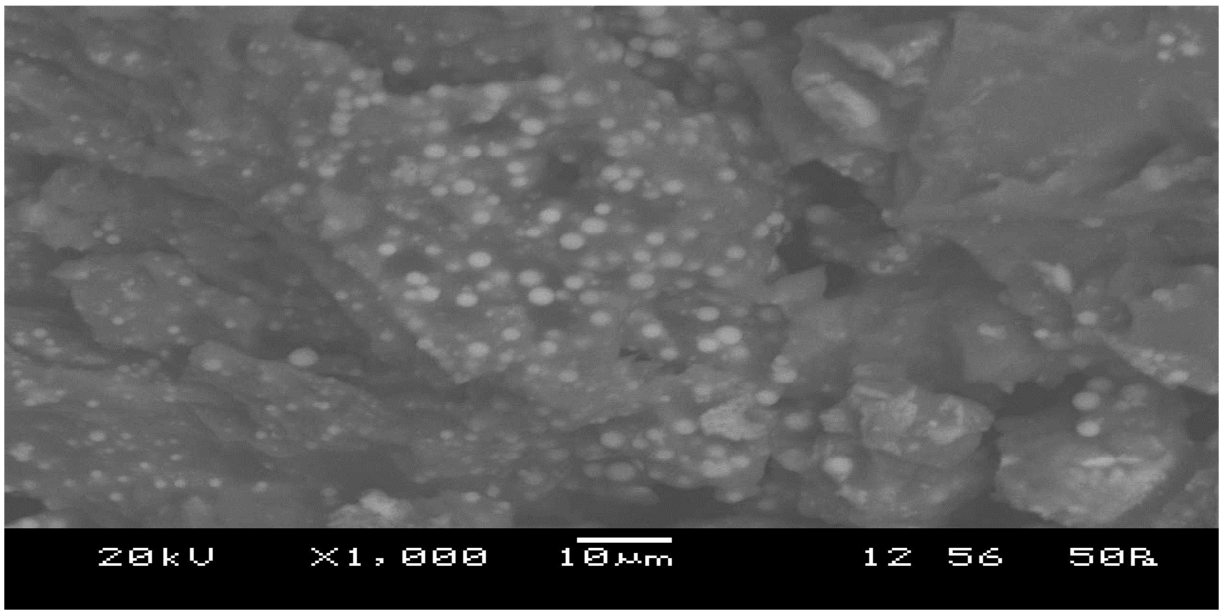

Figure 22 SEM image of sesame char taken at 1,000X magnification.

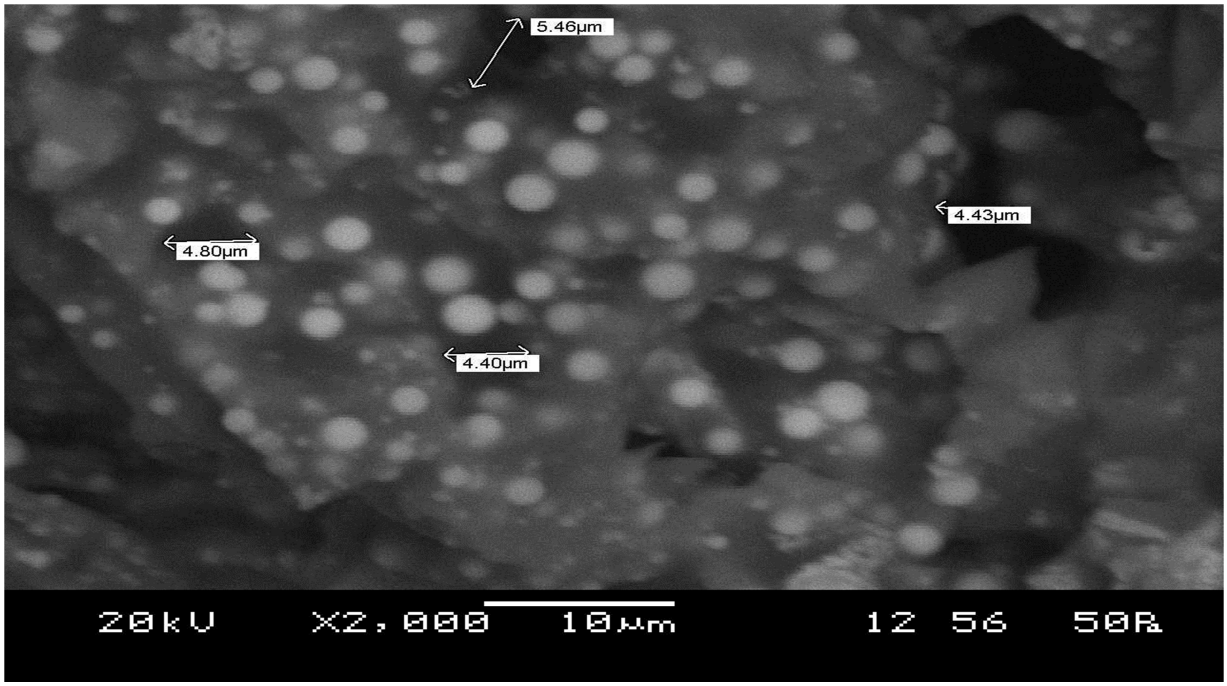

Figure 23 SEM image of sesame char taken at 2,000X magnification.

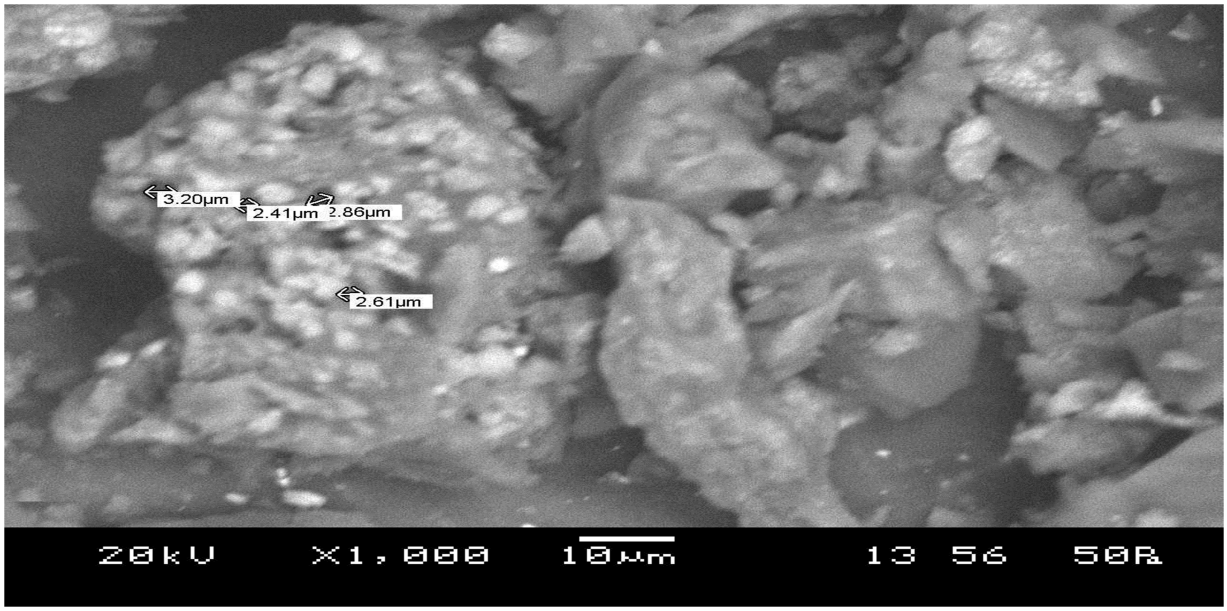

Figure 24 SEM image of groundnut char taken at 1,000X magnification.

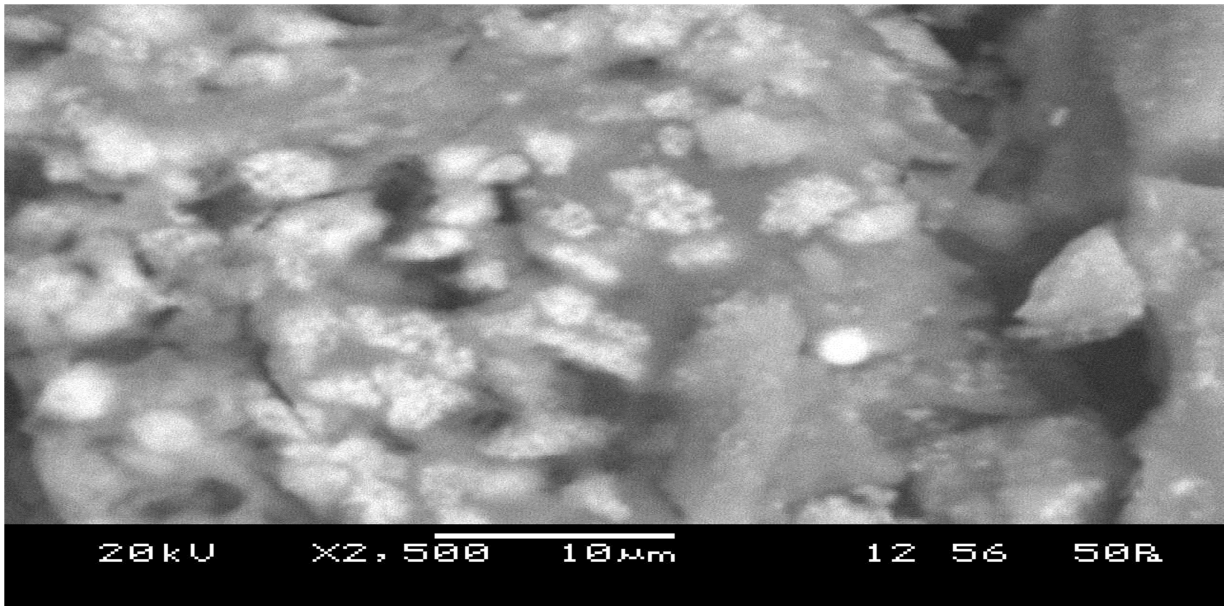

Figure 25 SEM image of groundnut char taken at 2500X magnification.

Analysis with EDX of sesame char surface shows the presence of C (71.48%), O (13.54%), as its major compositions. Figure 24 &25 are taken at 1000X and 2500X magnification for groundnut char. The average pore size on the surface groundnut char was found to be 3 µm. Presence of white colour spots on surface shows the presence of residual ash. EDX analysis of groundnut char showed the presence of C (74.78%), O (15.38%).Table.10 shows the results of EDX analysis. Figure.26 and 27 shows the EDX spectra of sesame and groundnut char.

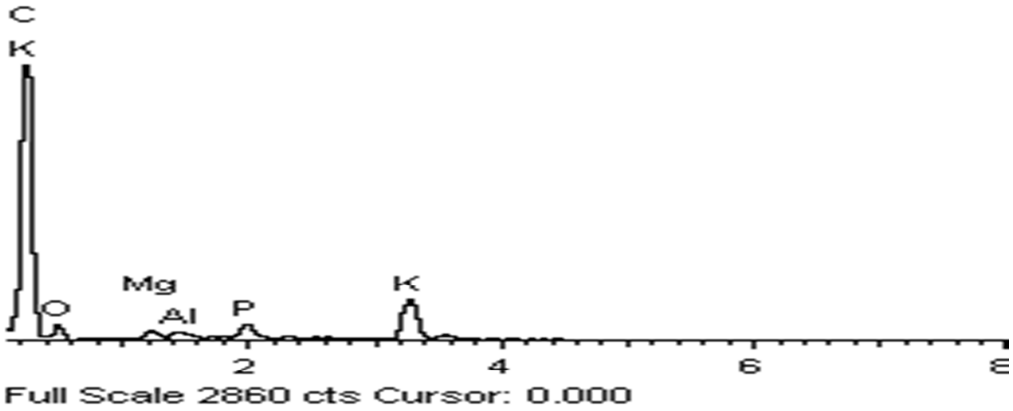

Figure.26 EDX spectra of sesame char.

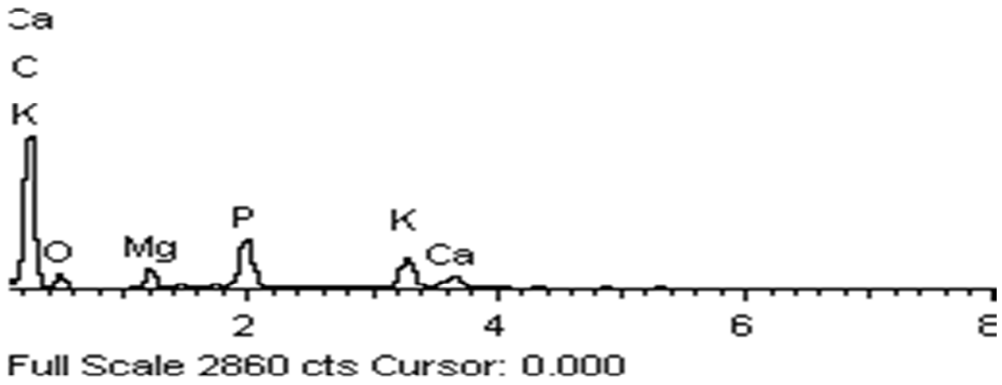

Figure.27 EDX spectra of groundnut char

Table.13 Results of EDX analysis of sesame and groundnut char.

Element	Sesame char (Weight %)	Groundnut char (Weight %)
C	79.17	71.48
O	13.54	15.38
Mg	0.68	1.95
Al	0.38	-
P	1.26	5.36
K	4.97	4.16
Ca	-	1.67

CHAPTER - 6

CONCLUSION

6. CONCLUSION

Demand for energy and its resources, is increasing every day due to the rapid growth in population and industrialization. It is necessary to get a process which can convert biomass into useful energy products especially to liquids which can be a good substitute for the depleting fossil. Pyrolysis is one such process and it has received special attention as it can convert biomass directly into solid, liquid and gaseous products by thermal decomposition of biomass in absence of oxygen.

In the present report, pyrolysis experiments on sesame seed and groundnut seed have been done and liquid yield was highest at 500^0Chaving 58.97 Wt %and 70.95 Wt % of oil recovery respectively. With increase in temperature, reaction time and weight of char decreased. Volatiles initially decreased and then increased with increase in temperature.

The different FTIR spectra of sesame and groundnut oil show the presence of mostly alkane and alkenes. The results were found consistent when compared with the results of GC-MS.

1H NMR analysis of bio-oil proves that β- CH_3, CH_2 hydrogen protons are attached to an aromatic ring in higher proportions.

Presence of pores shown by SEM-EDX analysis paves a path for using this char as an adsorbent.

Preliminary tests using thermal pyrolysis were promising and confirmed the feasibility of converting such seeds to liquid products. These liquid products have compositions overlapping those of major existing hydrocarbon fuels such as petrol; diesel and kerosene. Use of these products directly as a fuel or for reprocessing in a refinery therefore appears possible. The study performed has provided important information showing that prospects for using small-scale simple pyrolysis processes to deal with sesame seed and groundnut seed appear good and further investigations are required by taking some suitable catalyst.

CHAPTER - 7

FUTURE WORK

7. FUTURE WORK:

1. Distillation of the obtained liquid product.
2. Kinetic study of the thermal pyrolysis by thermo gravimetric analysis
3. Engine performance of distilled liquid product

CHAPTER - 8

REFERENCES

8. **REFERENCES:**

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